Electron and Optical Spectroscopies of Graphene Nanoribbons: Insights from Ab-Initio Calculations

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Graphene nanostructures have striking properties related to the lateral confinement that can open a band gap and induce semiconducting behavior. Key features connected to the tunability of electronic and optical properties as a function of structural parameters, e.g. width and edge structure of graphene nanoribbons (GNR), have been predicted theoretically (see e.g. [1-2]); however, only recently atomic control of GNR geometry (orientation, width and edge termination) was demonstrated [3]. These advancements in the fabrication procedure have thus allowed the first measurements of the band gap and the topology of the occupied bands of atomically precise armchair GNRs (AGNR's) by scanning tunneling spectroscopy (STS) and angle-resolved photoelectron spectroscopy (ARPES) techniques [4].
In this work we combine cutting edge theoretical and experimental techniques to study the electronic structure of a specific armchair nanoribbon (N=7, 7-AGNR). In particular we compare many-body perturbation theory calculations (performed at the GW level) with ARPES and STS data.

First principles calculations based on Density Functional Theory (DFT) were carried out for 7-AGNR, both isolated and on Au(111) substrate. Our findings clearly show a weak interaction between 7-AGNR and the Au(111) metal substrate. In order to compare ARPES and STS experiments, we have computed the self-energy corrections to the electronic structure by means of many-body perturbation theory, within the so-called GW approximation, which brings the gap to 3.7 ± 0.1 eV (the LDA value is 1.6 eV) [1]. We then estimated the gap reduction due to the presence of the metallic substrate by adding an image charge (IC) correction to the GW energy gap of the isolated GNR. Overall, this results in a theoretical estimate of the energy band gap of 2.3 to 2.7 eV for the 7-AGNR on Au(111), which is in very good agreement with the experimental value of 2.3 ± 0.1 eV.

The above results show that our ab-initio theoretical scheme can provide quantitative predictions for electron spectroscopies of nanoribbons on weakly coupled substrates such as Au. Recent results for optical excitations and excitonic effects will also be discussed, including the spectral evolution from molecular and polymer precursors to nanoribbons.

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