Excitations in graphene nanostructures

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Recent experimental advances have shown that atomically precise ultranarrow graphene nanoribbons can be realized with extreme control on size and edge configuration [1], and the first measurements by scanning tunneling and angle-resolved photoelectron spectroscopies confirmed theoretical predictions on the band gap and the topology of the occupied bands [2].

Here we discuss the key features of quasiparticle energies and optical excitations in graphene nanostructures as predicted by means of the ab-initio GW-BSE approach [3] and by simplified schemes to treat complex structures [4] and substrate effects [2].

We show that huge exciton binding energies and controlled charge transfer excitations can be obtained by designing appropriate nanoribbon structures. Based on this analysis, we then compare with the results of very recent differential reflectance spectroscopy (RDS) experiments of graphene ribbons on Au substrates, indicating that this theoretical scheme can provide quantitative predictions for electron and optical spectroscopies of nanoribbons on weakly coupled substrates.

The combination of RDS and ab initio simulations beyond DFT allows us to catch nanoribbons in the act of their formation, following the build-up of their quasi-1D excitons. In fact, the main phases observed by RDS on Au –from isolated molecular precursors to the final nanoribbon structure obtained by intramolecular cyclodehydrogenation— are characterized by distinct signatures that we can assign to excitonic states with very different binding energies, a clear manifestation of the modified electron/hole localization and interactions induced by the changes in intermolecular bonding and conformation during the formation process.

Work performed with A. Ferretti, D. Prezzi, A. Ruini and Shudong Wang. We have enjoyed the experimental collaborations with P. Ruffieux and coworkers (Zürich), K.H. Müllen and coworkers (Mainz) and R. Denk and coworkers (Linz).

This talk is dedicated to the memory of Rodolfo Del Sole, a great theorist and friend who introduced me to some of the mysteries of surface optical spectra a long time ago.

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