Many-body interactions and optical excitations in graphene nanostructures*

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Abstract

Graphene nanoribbons display extraordinary optical properties due to quantum-confinement, such as width-dependent bandgap and strong electron–hole interactions, responsible for the formation of excitons with extremely high binding energies. We show that our ab-initio simulations [1] based on many body perturbation theory (GW+BSE) can provide accurate quantitative predictions of electronic [2] and optical [3] properties in ultranarrow, structurally well-defined ribbons obtained by on-surface synthesis, once substrate effects are properly taken into account.

We further investigate the effects of many-body interactions through guide-function quantum Monte Carlo model calculations, and find huge biexcitonic effects, which are expected to play a role in high-intensity photoexcitation regimes. Femtosecond transient absorption spectroscopy measured as a function of the excitation fluence [4], performed in solution on well-characterized nanoribbons [5], indeed shows the impact of enhanced Coulomb interaction on the excited states dynamics: In the high-excitation regime, biexcitons form with high efficiency by nonlinear exciton-exciton annihilation, and radiatively recombine via stimulated emission [4]. The strong stimulated emission signal observed from biexciton states is promising in view of using nanoribbons as active light-amplifying materials, and suggest that also multiple-exciton generation –governed by the same exciton-exciton annihilation rate- can be extremely efficient in these systems.

Multi-particle excitations --excitons and biexcitons--, arising from extreme quantum confinement, thus dominate both the linear and non-linear optical spectra of graphene nanoribbons. A careful description of Coulomb interactions, including edge, substrate and dielectric screening effects, is required for their full understanding.

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