Ab-initio approaches based on Green's function theory became a standard tool for quantitative and predictive calculations of linear response optical properties in Condensed Matter. In particular, the state-of-the-art approach proved to effectively and accurately account for the essential effects beyond independent particle approximation (IPA) in a wide range of electronic systems, including extended systems with strong electron-hole interaction. In contrast, for non linear optics *ab-initio* calculations of extended systems rely in large part on the independent particle approximation. We have developed a new approach to study the non-linear response of solids based on a real-time propagation of an effective Schrödinger equation that allows to calculate response functions beyond the linear one including correlation effects. We applied this new methodology to study semiconducting two-dimensional (2D) materials.

Optical properties of bulk material are usually studied in frequency domain, by means of different approaches based on the linear response theory. While these approaches allow to include different effects beyond the independent particles approximation in the response functions, they are difficult to extend beyond the linear response regime.

For this reason in our work we decided to switch from the frequency domain to the time one.

The time-domain approach presents three major advantages with respect to frequency-domain response-based approaches. First, many-body effects are included easily by adding the corresponding operator to the effective Hamiltonian. Second, it is not perturbative in the external fields and therefore it treats optical susceptibilities at any order without increasing the computational cost and with the only limitation dictated by the machine precision. Third, several non-linear phenomena and thus spectroscopic techniques are described by the same equation of motions. For instance, by the superposition of several laser fields one can simulate sum- and difference-frequency harmonic generation, or four-waves mixing.[1]

In our approach correlation effects are derived from the Green's function theory, in the so called GW plus Bethe-Salpeter approximation.

We applied all these advances to study non-linear optical response of two-dimesional crystals. These materials exhibit unusual optical properties that can be exploited for novel optoelectronics ranging from flexible photovoltaic cells to harmonic generation and electro-optical modulation devices. Rapid progress of the field, particularly in the growth area, is beginning to enable ways to implement 2D crystals into devices with tailored functionalities. For practical device performance, a key challenge is to maximize light matter interactions in the material, which is inherently weak due to its atomically thin nature. Light management around the 2D layers with the use of plasmonic nanostructures can provide a compelling solution. We have shown that correlation effects can enhance the non-linear response of these materials by more than 200%.[2]

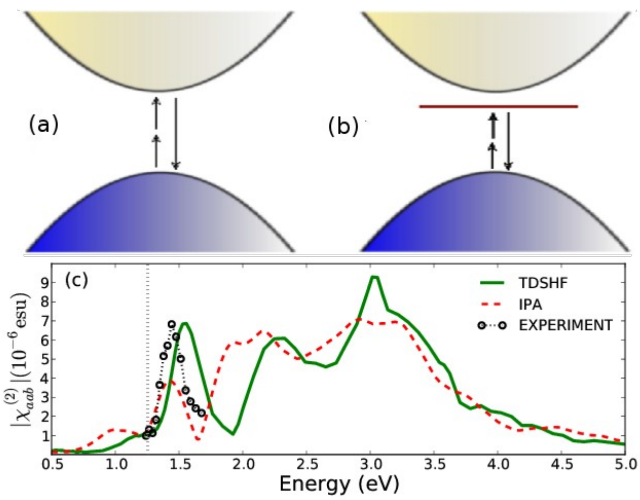

Fig. 1: Second Harmonic Generation: a) simplified picture of the second harmonic generation without bound excitons; b) second harmonic generation in presence of excitons c) SHG results for MoS_2 monolayer, comparison of the theory with and without excitonic effects and experiments

In Fig 1 we report the second-harmonic generation in MoS2, compared with recent experiments results. Since these effects depend from the screening of the electron-electron interaction, combining layers of different materials open the possibility to tune this screening and so the non-linear response.

References:

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