The theoretical description of nonlinear optical spectroscopy has traditionally been laid in the framework of perturbation theory. Within this formalism, an intuitive approach to the understanding of the dynamics of a molecular system excited by several external laser pulses is based on the concept of nonlinear response functions. However, as the system complexity increases or nontrivial dynamic effects have to be taken into account (nonadiabatic interstate couplings, bath-induced relaxation) the perturbative approach becomes computationally expensive. To tackle this scenario nonperturbative approaches based on the numerically exact solution of quantum equations of motions have been developed.

In this talk, I will demonstrate how the nonperturbative approaches can be efficiently applied to two different problems of femtosecond molecular spectroscopy.

In the first part of my talk, I will concentrate on the spectroscopic elucidation of ultrafast electron-transfer processes. To this end, I consider a model of a spectroscopically accessible avoided crossing formed by the lowest two excited singlet states in the vicinity of the Franck-Condon region of a polyatomic molecule, augmented with a higher excited electronic state. The considered system reaction mode is coupled to a harmonic bath, which is responsible for the relaxation dynamics. The electronic interstate-coupling is assumed strong, so that the electron-transfer dynamics deviates from the Fermi-Golden behavior, showing electronic and vibrational beatings. A comprehensive mapping of the nonadiabatic wave packet dynamics in such a system calls for the application of several complementary spectroscopic techniques. I simulate with computational methods the outcome of such a concerted experimental effort and compute the signals of four well-established two-pulse spectroscopies.
time and frequency resolved fluorescence, transient absorption pump-probe and femtosecond stimulated Raman spectroscopy. The simulations are based on an exact numerical solution of the driven time-dependent multi-state Redfield master equation [1]. The effects of laser pulse shape and pulse overlap are fully included. We demonstrate which features of the photoinduced dynamics, such as electronic/nuclear populations, electronic/nuclear coherences or electronic/nuclear charge transfer processes are imprinted in the simulated signals. It will be shown that a fairly complete and systematic picture of the coupled electronic/nuclear dynamics at avoided crossings can be obtained in this manner.

The second part of my talk deals with the simulation of nonlinear signals beyond the regime of weak system-field coupling. I will focus on the theoretical description, interpretation and information content of double-pump femtosecond single-molecule signals of individual chromophores in the weak-field regime [2] and in the strong-field regime [3].


Host: Angel Rubio