Advances and future prospects in the theoretical evaluation of Nonlinear optical properties

Abstract

Reliable predictions of electronic and vibrational (hyper)polarizablilities are critical for the rational design of materials possessing large nonlinear optical (NLO) response. Due to a large effort by several groups, the prominent role of the vibrational contributions in many instances is now well-established. However, their calculation can pose difficulties in particular cases and computational methods to deal with such instances effectively are still under active development. For chemical systems with large amplitude modes in a several-minimum potential well, the energy cannot be expanded in the usual power series in the field used to define the electric hyperpolarizabilities. Then, the nonlinear properties cannot be evaluated using the existing approaches. In this seminar, a method for computing the nonlinear optical properties of molecules with arbitrary double well potentials is presented. It is also shown that this new approach can also be used to evaluate the vibrational Stark effect spectroscopy (VSES) of such very anharmonic systems. Furthermore, we will also show present several results that point that none of the most common used functionals perform satisfactorily for the calculation of the electronic and vibrational (hyper)polarizabilities.