Modelling molecules in electric and magnetic fields

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The study of molecules in electric and magnetic fields is gaining increasing theoretical interest, due to the possibilities offered by nonlinear optics in designing functional materials with superior properties for use for instance in three dimensional optical data storage, microfabrication, optical power limiting, upconverted lasing, fluorescence imaging, and photo-dynamic therapy. Added control comes also from involving vibrational excitations as well as the possibilities of exploring the magnetic component of the electromagnetic light, leading to a range of chiroptical spectroscopies and birefringences.

A challenge for the theoretical study of such nonlinear phenomena involving electronic and vibrational degrees of freedoms for molecules exposed to electric and magnetic fields is the high order of the molecular properties and the fact that the basis set depends explicitly on the positions of the nuclei and also on the external magnetic field if Gauge-Including Atomic Orbitals (GIAOs) are used.

In the lecture, I will outline the main features of a new approach we have developed for the calculation of higher-order frequency-dependent molecular response properties using perturbation-dependent basis sets for self-consistent field states and wave functions. A novelty of the approach is the fact that the theory is formulated fully in the atomic orbital basis, allowing us to take advantage of recent advances in linearly scaling computational methodology. Being formulated in the atomic orbital basis, the formalism is also easily extended to two- and four-component relativistic SCF methods.

The main part of the lecture will focus on showing different applications of the methodology, demonstrating both how theory may aid experimental analysis, as well as give examples where agreement between theory and experiment is still lacking. Particular attention will be given to nonlinear vibrational spectroscopy and different Raman scattering processes in particular, but examples of nonlinear optical properties as well a birefringences will be given.