Real-time theoretical description of coherent electronic dynamics probed by high-harmonic generation and chiral spectroscopies

Eleonora Luppi

Laboratoire de Chimie Théorique, Sorbonne Université Paris France

ABSTRACT

The interaction of molecules with ultrafast electromagnetic fields induces coherent electronic dynamics that can be probed through a variety of nonlinear and chiral spectroscopies. High-harmonic generation (HHG) and electronic circular dichroism (ECD), despite probing different observables, both originate from the time-dependent coherent response of the electronic wavefunction to an external field. In particular, these spectroscopies provide complementary access to electronic populations, coherences, and orbital contributions, through the time-dependent electric and magnetic dipole moments.

In this contribution, I will present a real-time theoretical framework based on the propagation of the electronic wavefunction under external electromagnetic fields. This approach enables the simulation of both high-harmonic generation (HHG) spectra and electronic circular dichroism (ECD) signals from first principles, providing direct insight into the role of electronic structure, coherence, and transition dipole dynamics.

For HHG, I will show how the emitted harmonic spectra encode detailed information on orbital-resolved contributions, electronic coherence, and symmetry properties of the molecular system. In particular, the analysis reveals the role of multiple ionization channels, interference between electronic states, and the influence of molecular symmetry and chirality on the harmonic emission. This provides a microscopic interpretation of strong-field electron dynamics and the origin of characteristic spectral features.

For ECD, I will demonstrate how chiral optical signals arise from the coherent electronic response and how they are modified by environment-induced interactions, such as coupling with plasmonic nanostructures. Applications to molecular systems and plasmon–molecule coupled systems show how electronic coherence and environment effects influence the chiral optical response.

These results highlight the potential of real-time theoretical approaches to interpret advanced nonlinear and chiral spectroscopies and provide a unified microscopic description of ultrafast electronic and chiral dynamics in molecular systems.