Combined First-Principles and Machine-Learning Approach to Real-Time Nonlinear Spectroscopies

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Outline: Second Harmonic Generation (SHG) is a nonlinear spectroscopic technique which measures the response of a material at twice the incident laser frequency. SHG is highly sensitive to the changes in local electric fields that may arise from e.g. local symmetry breaking, polarization, and crystallographic orientation. SHG is used as a probe for ultrafast carrier dynamics in excited electronic systems: the system is excited by a pump laser and later the SHG is measured with a probe laser. This technique, which is referred as time-resolved SHG, has been applied, for example, to investigate ultrafast ferroelectricity, antiferromagnetic domain manipulation, hot-electron transfer, high-order excitonic and the non-radiative energy transfer from exciton to phonon. Due to the wealth of phenomena playing a role at the picosecond timescale and below, the interpretation of these experiments is usually difficult. First-principles modelling can in principle help the interpretation of these experiments. In this case, the challenges come from the theoretical complexity and the computational cost of simulating a system out-of-equilibrium. In recent years, machine-learning (ML) has become an increasingly popular method to circumvent electronic structure theory calculations, instead making use of the fact that the properties of materials are smooth functions of the atomic positions. ML approaches represent a promising way to access first-principles results and thus an accurate experimental analysis with a much smaller computational effort.

This project aims to model time-resolved SHG experiments from first principles and machine learning. This would provide a computational tool to simulate time-resolved SHG that can be directly compared with experiments so to offer a detailed microscopic interpretation. The project will involve theoretical work, coding and running simulations. The Yambo code [1], which implements first-principles approaches to simulate both SHG and pump-probe experiments will be used; the librascal code for converting atomistic configurations into features for input into machine-learning algorithms will also be used [2], and some development of methods for learning the polarization of materials will be a part of the project.

References:

[1] D Sangalli *et al* 2019 *J. Phys.: Condens. Matter* **31** 325902

[2] Deringer *et al* 2021 *Chem. Rev.* **121** 10073