

**Density functional theory for simulating core spectroscopy:
Problems, solutions and applications.**

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Core spectroscopy is undergoing rapid experimental progress, associated with new light sources, and improvements in time resolution. Together with the inherent element-specificity and atomic site specificity of x-ray absorption spectroscopy (XAS), this makes UV-visible pump / XAS probe experiments a powerful tool to follow reactive chemical dynamics in real time. There is accordingly a growing need for efficient and reliable simulation methods to predict XAS spectra of molecules in their ground and excited states using quantum chemistry methods.

This talk will discuss recent progress made in my group in developing and applying density functional theory (DFT) approaches to simulating XAS spectra. The motivation for this research is the fact that standard linear response time-dependent DFT (TDDFT) exhibits very serious problems for XAS. The origin is in the standard adiabatic approximation, which leads to lack of orbital relaxation (in common with charge-transfer excitations). I will then discuss two alternatives under active development in my group (and also elsewhere).

First is the use of state-specific orbital-optimized DFT (OO-DFT), which corresponds to finding saddle points of a ground state functional, without making the adiabatic approximation or doing linear response at all. A series of tests and examples shows that OO-DFT resolves most of the major problems of TDDFT for modeling XAS in terms of quality of results, although it is not as convenient to use because of the need to simulate each individual state that contributes to a given spectrum. Second is the possibility of resurrecting the ease of use of TDDFT, whilst correcting the major problems associated with the adiabatic approximation. Some exciting recent progress will be discussed. To show the promise of these approaches for modeling chemistry, some results from recent collaborations with experimental groups will be shown, illustrating the promise of observing (and simulating) reactive chemistry with time-resolved XAS.

Like so many of the projects performed in my group, this work would simply not have been possible without the students and postdocs who have made it happen. It is my pleasure to acknowledge my gratitude to Diptarka Hait, Leo Cunha, Kevin Carter-Fenk, Katherine Oosterbaan, and Juan Arias in the context of this specific topic, whilst also honoring earlier group members who placed their creative stamp as well as great effort, into so many previous projects. It is also a pleasure to thank the conference organizers for making MQM 2022 happen!