

X-ray spectroscopy from 2- and 4-component relativistic damped linear response theory

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X-ray spectroscopy provides a wide range of different methods for exploring the electron density of molecules. Its versatility is due to the fact that it allows to probe both core and valence orbitals. From a computational point of view, X-ray spectroscopy is challenging, as it requires a uniformly accurate description of both core and valence orbitals and an accurate description of highly excited electronic states. The core orbitals will also be significantly affected by relativistic effects, both through scalar relativistic effects as well as the spin-orbit splitting of degenerate p and d core orbitals, leading to L_{2/3} and M_{4/5} edges in X-ray absorption spectroscopy. Accessing highly excited electronic states is by itself challenging, but in many cases made more difficult due to the spurious appearance of non-physical excited states arising due to the use of finite basis sets. When time-dependent density-functional theory is applied, an added complication is self-interaction errors due to the approximate nature of the exchange-correlation functional.

In this talk, I will describe our recent work towards fully relativistic calculation of different X-ray spectroscopies based on 2- and 4-component damped linear response theory [1]. This allows the specific energy ranges to be efficiently addressed, and in combination with selected excitation windows and using a multifrequency linear response solver, we can ensure both computational efficiency and that only physically meaningful states are accessed. I will also demonstrate that the exact 2-component (X2C) approximation leads to near-perfect agreement with the full 4-component results, with significant computational savings.

I will in the talk present some of our latest results of the methodology for different X-ray spectroscopic processes. Particular attention will be given to a recent study of L_{2,3}- and M_{4,5}-edges of closed-shell transition metal and actinide compounds with different central atoms, ligands, and oxidation states [2]. The full inclusion of relativistic effects allows us to disentangle errors in conventional DFT studies due to self-interaction errors and the approximate treatment (or neglect of) relativistic effects. I will show that by a careful calibration of the amount of exact Hartree–Fock exchange used in hybrid DFT functionals, we can obtain excellent agreement with experimental observations at the 4-component TDDFT level of theory without the need of shifting the onset of near-edge X-ray absorption bands, as is commonly done in computational studies of X-ray absorption bands.

[1] *Relativistic four-component linear damped response TDDFT for electronic absorption and circular dichroism calculations.* L.Konecny, M.Repisky, K.Ruud and S.Komorovsky, *J.Chem.Phys.* 151, 194112 (2019).

[2] *Accurate X-ray absorption spectra near L- and M-edges from relativistic four-component damped response TDDFT.* L.Konecny, J.Vicha, S.Komorovsky, K.Ruud and M.Repisky, *Inorg.Chem.* 61, 830-846 (2022).