Modeling core spectroscopy of heavy elements: the role of orbital relaxation and relativistic effects

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X-ray spectroscopy is widely used to study local chemical environments by probing the electronic structure of the innermost orbitals and obtaining element specific spectral signatures.[1,2] Theory can assist in interpreting these features, but accurate modeling requires a description of orbital relaxation effects that are crucial for characterizing the core-hole. Moreover, as we explore elements of the periodic table with higher atomic numbers, relativistic effects become more relevant, especially for the prediction of K (1s) and L (2p) shell transitions.

We combine the exact two-component one electron model (X2C)[3,4] for relativistic effects with two DFT based approaches to study K-edge X-Ray spectroscopies for elements of the third row and early transition metals of the periodic table. The first approach is based on optimizing an excited state configuration directly, within the framework known as orbital-optimized (OO) DFT.[5] The second approach, electron-affinity TDDFT (EA-TDDFT), relies on a double linear-response on top of a core-ionized reference, and attempts to fix the shortcomings of regular TDDFT for core-spectroscopy.[6]

Both OODFT and EA-TDDFT, when combined with X2C, show remarkable agreement in predicting K-edge X-Ray absorption spectra of a wide range of molecules containing third row main group elements, with RMSE < 0.5 eV. We also investigate how higher order relativistic effects, such as retardation and vacuum fluctuations, play a significant role in the core binding energies of transition metals and how this affects the accuracy of our proposed methods. Finally, we also present some progress on modeling spin-orbit effects and L-edge spectroscopy within the X2C framework.

[1] *Nano Lett.* 2007, 7, 4, 905–909.

[2] *Acc. Chem. Res.* 2015, 48, 11, 2967–2975.

[3] *J. Chem. Phys.* 2007, 126, 064102.

[4] *J. Chem. Phys.* 2009, 131, 031104.

[5] *J. Phys. Chem. Lett.* 2022, 13, 15, 3438–3449.

[6] *J. Phys. Chem. Lett.* 2022, 13, 41, 9664–9672.