

The role of the coupling matrix elements in TD-DFT simulation of core-level spectra of transition metal complexes

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Time-dependent density functional theory (TD-DFT) remains the premier choice when computing core-level spectra due to its ability to produce reasonably accurate spectra with acceptable computational cost. However, in the computation of transition metal complexes, TD-DFT is still limited to smaller systems which necessitates the exploration of further approximations. Following in the footsteps of Visscher, Aikens, and others applying semi-classical approximations towards valence excited states, we explore how similar approximations can be made to describe core-level excited states. In this study we evaluated the role of the Coulomb, Hartree-Fock exchange, and exchange-correlation kernel contributions to the TD-DFT coupling matrix in the simulation of core-level spectra in transition metal complexes. Surprisingly, the exchange-correlation kernel, which makes up the majority of the computational cost, has a marginal effect on the simulated spectra. The Coulomb term also has little impact on the K, L_1 , and $M_{4,5}$ edges but plays a larger role in the simulation of the $L_{2,3}$ edge. Finally, our results confirm that the Hartree-Fock exchange term is the most important term and should not be neglected. Additionally, the aforementioned observations hold true regardless of basis set and exchange correlation functional. The result of our study suggest that for specific cases, there is no profit in including every term of the coupling matrix elements. This provides a promising avenue for further optimization of core-level spectra simulation and a more in-depth understanding in the mechanisms behind such calculations.