Core-Hole Initiated Charge Migration with TDDFT

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Abstract: Attosecond electron dynamics in molecules underpins a range of important processes such as light harvesting, photochemistry, and ultrafast spectroscopy. Modeling these dynamics from first principles is important for predicting and interpreting ultrafast experiments. In the case of large molecules, however, correlated techniques can be prohibitively expensive. Here, time-dependent density functional theory (TDDFT) offers a promising alternative, but limitations in the exchange-correlation functional, especially the adiabatic (local-in-time) approximation limit the accuracy of the results.

In this talk, I will present a study demonstrating the validity of TDDFT for core-hole triggered charge migration in nitrosobenzene. Specifically, by initializing the system with an unambiguous initial state (a nitrogen K-edge core-hole), real-time TDDFT with hybrid functionals captures hole migration across the molecule with accuracy comparable to ADC(4) [1]. These results suggest that given an initial state that is a good reflection of a molecule after interaction with a exciting or ionizing pump field, adiabatic TDDFT adequately capures the dynamics.

References

[1] Alexander I. Kuleff, Nikolai V. Kryzhevoi, Markus Pernpointner, and Lorenz S. Cederbaum, "Core Ionization Initiates Subfemtosecond Charge Migration in the Valence Shell of Molecules", *Phys. Rev. Lett.* **2016** *117*, 093002