Contribution ID : **133** Type : **Poster Presentation**

EuCompChem2025 Pierpaolo D'Antoni Oral

Description of Charge-Transfer states for large systems by Range Separated functionals within polTDDFT

Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L. Giorgieri 1, Trieste, Italia

PIERPAOLO.D'ANTONI@phd.units.it

Time-dependent density functional theory (TDDFT) has become the method of choice for simulating the optical properties of large molecular systems. Its favourable computational scaling and good accuracy, combined with ongoing efforts to improve algorithmic efficiency, are paving the way for the theoretical characterization of increasingly large and complex systems. Among the available schemes, PolTDDFT stands out for its balance between accuracy and computational cost [1]. Despite being formally exact, (TD)DFT relies on approximations for the exchange-correlation (xc) functional, whose exact form remains unknown. These approximations are responsible for known limitations of the method, most notably, its poor description of charge-transfer (CT) states. Head-Gordon, Weisman, and Dreuw were among the first to demonstrate that local xc functionals fail to capture non-local interactions like the electrostatic attraction between spatially separated charges in long-range CT excitations [2]. To overcome this issue, range-separated (RS) hybrid functionals were introduced, incorporating a distance-dependent fraction of exact Hartree–Fock exchange. In this work, we integrate the use of a RS functional (CAMY-B3LYP [3]) into the PolTDDFT/fitted-HDA computational framework [4] to address both the challenges of computational efficiency and accurate CT-state description. We assess the performance of our implementation by simulating the optical response of a well-known Donor–Acceptor–Acceptor triad [5] and comparing the results to both the benchmark Casida formulation of TDDFT and available experimental data.

[1] O. Baseggio, G. Fronzoni, M. Stener, J. Chem. Phys., 2015, 143, 024106.

[2] A. Dreuw, J. Weisman, M. Head-Gordon, J. Chem. Phys., 2003, 119, 2943- 2946.

[3] M. A. L. Marques, M. J. T. Oliveira, T. Burnus, Comput. Phys. Commun., 2012, 183, 2272.

[4] P. D'Antoni, M. Medves, D. Toffoli, A. Fortunelli, M. Stener, L. Visscher, J. Phys. Chem. A, 2023, 127, 9244.

[5] C. B. Larsen, O. S. Wenger, Angew. Chem. Int. Ed. 2018, 57, 841.

Primary author(s) : Mr. D'ANTONI, Pierpaolo (Dipartimento di Scienze Chimiche e Farmaceutiche Università degli Studi di Trieste); Prof. STENER, Mauro (Dipartimento di Scienze Chimiche e Farmaceutiche Università degli Studi di Trieste)

Presenter(s) : Mr. D'ANTONI, Pierpaolo (Dipartimento di Scienze Chimiche e Farmaceutiche Università degli Studi di Trieste)