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Assessing the fitness of various exchange-correlation functionals for TD-DFT studies of charge-transfer excitations in organic dyes[1]

PRATIBHA DEV, SAURABH AGRAWAL, NIALL ENGLISH, School of Chemical & Bioprocess Engineering, University College Dublin, SEC STRATEGIC CLUSTER TEAM — Dye Sensitized Solar Cells (DSSCs) are a possible alternative to the more expensive silicon-based cells. Theoretical research in this field has highlighted some of the issues with time-dependent density functional theory (TD-DFT) that is widely used to study electronic excitations of matter. The situation is complicated by the fact that several classes of approximations to the exchange correlation functional can be employed, however, not one of these strictly outperforms the others in its description of charge-transfer excitations. In this work, UV-Vis spectra are calculated using TD-DFT for several organic dyes – alizarin, squaraine, 4-(N, N-dimethylamino) benzonitrile, polyene-linker dyes and triphenylamine-donor dyes. We studied the dyes within three approximations (PBE, B3LYP and CAM-B3LYP) to the exchange-correlation functional. In the dyes considered here, a correlation exists between the functional performance and the spatial overlap of the states involved in the excitations. This overlap can be quantified to provide a good guideline for choosing the right functional when studying intramolecular charge transfer in dyes. It will be an invaluable tool when studying these molecules within more challenging systems, such as dye-titania complexes in DSSCs.

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