

D_{CT}: A useful tool for the characterization of charge transfer excited states from small organic molecules to large metal complexes.

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Through-space charge transfer (CT) excitations play a key role in many technological applications from solar-to-electricity conversion devices to artificial and natural photosynthetic architectures. Defining the extension associated to an electronic transition is of particular relevance, especially in the case of charge-transfer (CT) excitations. Here we present a TD-DFT study, intended to provide a simple understanding and characterization of excited-state CT processes. We rely on the D_{CT} index, which recovers the effective charge/hole distance associated to a given transition, based on the computed ground state and excited state relaxed or unrelaxed densities. We first assess the reliability of the D_{CT}^[1,2], by simulating a large set of Donor-Acceptor (D/A) push-pull molecules derived from an α,ω -nitro-aminophenylene: For a given D/A pair, we study the evolution of the D_{CT} as a function of the length of the central spacer. In particular the "relaxed" (^RD_{CT}), unlike its "unrelaxed" (^UD_{CT}) counterpart is a measure of the redistribution of the electronic charge due to the excitation^[3]. Combining the use of ^RD_{CT} and ^UD_{CT} we inspect the character (CT or not) and the spatial extent of a given transition^[4]. Secondly we present a computational protocol, which allows to follow excited-state electron transfer in large metal complexes, based on the minimization of the D_{CT} index.

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