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An improved guess for the variational calculation of charge-transfer excitations in large molecular systems

An improved guess for the variational calculation of charge-transfer excitations in large molecular systems Nicola Bogoa, Zeyi Zhangb,c, Martin Head-Gordonb,c and Christopher J. Steina,d a) Department of Chemistry and Catalysis Research Center, TUM School of Natural Sciences, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany, christopher.stein@tum.de b) Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, USA. c) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA. d) Atomistic Modeling Center, Munich Data Science Institute, Technical University of Munich, 85748 Garching, Germany.

Photo-induced charge transfer (PCT) plays a fundamental role in biological systems and organic electronics, and also arises in synthetic nanostructured materials. Whereas the targeted preparation of molecular materials with pronounced PCT improved significantly over the last twenty years, the typical system size limits the application of accurate excited-state electronic structure methods for the analysis of PCT properties. Furthermore, efficient methods like time-dependent density functional theory (TD-DFT) are characterized by systematic errors when general-purpose exchange-correlation functionals (XCFs) are applied to the calculation of charge-transfer (CT) excitations, a deficiency that led to the development of specialized XCFs [1] for the calculation of CT excitations. In our previous publication, [2] we demonstrated how variational DFT methods, in particular orbital-optimized DFT (OO-DFT) methods [3], constitute the most accurate low-scaling electronic structure approximation for the calculation of inter-molecular CT excitations using a general-purpose XCF. Conceptually, a rigorous theoretical foundation has recently been proven for ΔSCF [4] approaches in line with previous work by Görling [5]. In the present work, we implement a freeze-and-release electronic structure algorithm [6] in the Q-Chem software package [7] to improve the convergence of OO-DFT calculations. The resulting electronic structure algorithm [8] is applied to the calculation of charge-transfer excitations in prototypical PCT systems with research applications in the field of organic semiconductors, namely a self-assembled Pd coordination cage [9] and two dye-semiconductor complexes [1]. We further discuss how the energies and properties change for different excited-state DFT methods and which reproduce the experimental results best.

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Primary author(s) :   BODO, Nicola (Department of Chemistry and Catalysis Research Center, TUM School of Natural Sciences, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany,)

Presenter(s) :   BODO, Nicola (Department of Chemistry and Catalysis Research Center, TUM School of Natural Sciences, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany,)