Electron Localization (Function) in the Excited State with Single Determinant Methods

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Since its first definition, back in 1990, the Electron Localization Function (ELF) has settled as one of the most commonly employed techniques to characterize the nature of the chemical bond in real space. Although most of the work using the ELF has been focused on the study of ground-state chemical reactivity, a growing interest has blossomed to apply these techniques to the nearly unexplored realm of excited states and photochemistry. Since accurate excited electronic states usually require to account appropriately for electron correlation, the standard single-determinant ELF formulation cannot be blindly applied to them, and it is necessary to turn to correlated ELF descriptions based on the two-particle density matrix (2-PDM). The latter require costly wavefunction approaches, unaffordable for most of the systems of current photochemical interest. Here, we compare exact, 2-PDM-based ELF results with those of approximate 2-PDM reconstructions taken from Reduced Density Matrix Functional Theory (RDMFT). Our approach is put to the test in a wide variety of representative scenarios, such as those provided by the lowest-lying excited electronic states of simple diatomic and polyatomic molecules. Altogether, our results suggest that even approximate 2-PDMs are able to accurately reproduce, on a general basis, the topological and statistical features of the ELF scalar field, paving the way toward the application of cost-effective methodologies, such as TD-HF or TD-DFT, in the accurate description of the chemical bonding in excited states of photochemical relevance.

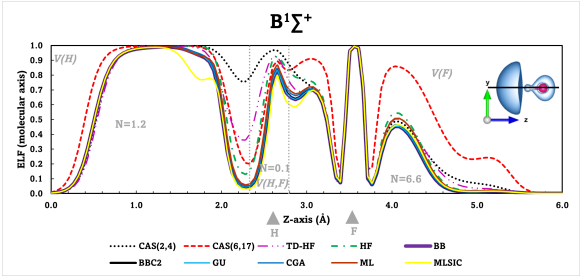

Figure 1: Profile of the electron localization function (ELF) along the internuclear axis in the Franck-Condon geometry of the second excited state, $B^1\Sigma^+$, of the hydrogen fluoride molecule.