

Using density descriptors to characterize electronic states: The case of doubly excited states.

Mariana T. do Casal^{1,2}, Josene M. Toldo², Mario Barbatti^{2,3} and Felix Plasser^{*4}

¹*KU Leuven, Leuven, Belgium*

²*Aix-Marseille University, Marseille, France*

³*Institut Universitaire de France, Paris, France*

⁴*Loughborough University, Loughborough, UK.*

Electronic states with partial or full doubly excited characters play a crucial role in many areas. This characterization is usually done by visually inspecting the most important molecular orbitals related to a specific state. In order to provide a more systematic analysis, several density descriptors based on the state density matrix, transition density matrix, and density difference matrix have been developed and extensively discussed for singly excited states [1] but less explored in the case of the elusive doubly excited states.

The prototypical example of doubly excited states is polyenes. However, although doubly-excited states have been studied in polyenes and related systems for many years, their assignment as single vs. doubly excited, even in simple polyenes, such as butadiene, has sparked controversies. So far, no well-defined framework for classifying doubly excited states has been developed, and even more, there is not even a well-accepted definition of doubly excited character. This work [2] presents a solution: a physically motivated definition of doubly excited character based on operator expectation values and density matrices, which works independently of the underlying orbital representation. Furthermore, we propose a classification scheme to differentiate two limiting cases: the open-shell and closed-shell doubly excited states. We illustrate the conversion between those two limiting cases using a well-known photochemical reaction, ethylene dimerization.

[1] Plasser, F.; Krylov, A. I.; Dreuw, A. *WIREs*, **2022**, 1–15.

[2] do Casal, M. T.; Toldo, J. M.; Barbatti, M.; Plasser, F. *Chem. Sci.* **2023**, *14* (15), 4012–4026.