The Particle-Hole Map: a Computational Tool to Visualize Electronic Excitations

The particle-hole map (PHM) is a new visualization tool to analyze electronic excitations in molecules in the time- or frequency domain, to be used in conjunction with TDDFT or other ab initio methods [1]-[3]. The purpose of the PHM is to give detailed insight into electronic excitation processes which is not obtainable from local visualization methods such as transition densities, density differences, or natural transition orbitals. The PHM provides information on the origins, destinations, and coherences of charge fluctuations during an excitation process. In contrast with the transition density matrix, the PHM has a statistical interpretation involving joint probabilities of individual states and their transitions, and it is easier to read and interpret. We present a derivation of the PHM from the two-particle reduced transition density matrix, discuss and illustrate its properties and numerical implementation, and give several examples and applications to charge-transfer excitations in organic donor-acceptor systems.

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