Electron localization as the information content of the conditional pair density

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Two information-based functions are proposed as a real space measure of the Fermi and Coulomb hole. The first one is the information content of the Exchange-Correlation hole, calculated from the Kullback-Leibler divergence of the same-spin conditional pair density respect to the marginal probability (the electron density). This information measure can be used to reveal the regions of the space associated to the classical electron pair model [1-3]. Here, correlated wave-functions, such as CISD, MP2, and CCSD, are considered. This is achieved by introducing an approximated method based on employing natural orbitals and their occupancy numbers [4]. In addition, we propose a measure of the information content of the correlation-hole, which is computed in terms of the Kullback-Leibler divergence of the correlated conditional pair-density respect to the uncorrelated Hartree-Fock pair density [5]. The methodology is discussed in the light of the result derived from noble-gas atoms, the F_2 molecule and some non-covalently bonded systems.

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