Analysis of electronic structure by maximal orbital decomposition

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We will describe the maximal orbital decomposition (MOD) approach that we use to analyze molecular orbitals in HF and DFT wavefunctions. The MOD method is based on the "corresponding orbital transformation" (COT) that is used to calculate the overlap between non-orthogonal wavefunctions.[1] Here the COT defines the 'best' overlap between any atom or fragment and the total *n*-electron molecular wavefunction. The approach takes advantage of the COT mathematical property that it maximizes (in Hilbert metric sense) any sub-trace of the overlap matrix. Accordingly, the MOD is 'maximal', there can be no better decomposition of the overlap between system and sub-system. We will show our initial applications of MOD to characterize chemical bonding in such prototypical systems as the water dimer, organo-metallic complexes, mixed-valent metal complexes, and lastly, hydrogen atom and proton-coupled electron transfer reactions.

(1) King, H. F.; Stanton, R. E.; Kim, H.; Wyatt, R. E.; Parr, R. G. Corresponding Orbitals and Nonorthogonality Problem in Molecular Quantum Mechanics. *Journal of Chemical Physics* **1967**, *47*, 1936.