

Contrasting Patterns of Delocalization in the Dyson orbitals of Aqueous Halides

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Abstract

Electron binding energies and corresponding Dyson orbitals of hydrated halide anions have been determined with *ab initio* electron propagator calculations that consider three, alternative descriptions of environmental effects. Calculations on microsolvated halides have been performed to demonstrate the efficacy of various self-energy approximations in capturing strong relaxation and correlation effects. The partial third-order and extended partial third-order self-energy approximations are especially efficient and accurate. Calculations on halides embedded in a first solvation sphere have employed model potentials to represent averaged, long-range hydration effects. A third approach obtains electron binding energies and local densities of states that are averaged over many solvent configurations produced by Monte-Carlo simulations with classical potentials. For most halides, the lowest electron detachment energies pertain to halide-centered valence p atomic orbitals and are followed by transitions to states with solvent-delocalized holes. This conclusion establishes the existence of final states which exhibit a solute-solvent charge transfer. However, in the case of fluoride, another picture emerges in which Dyson orbitals for the lowest electron detachment energies are not chiefly localized on the halide. In fact, Dyson orbitals with large fluoride contributions also have equally large amplitudes on nearby solvent molecules.

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