Electron Propagator Calculations on the Photoelectron Spectra of Aqueous Halides

J. V. Ortiz
Department of Chemistry and Biochemistry
Auburn University
Auburn, Alabama 36849-5312

2012 Sanibel Symposium

Abstract

Electron binding energies and corresponding Dyson orbitals of solvated anions have been examined with *ab initio* electron propagator calculations on clusters that are embedded in a model electrostatic potential. Spectral predictions represent averages over solvent configurations that are generated by Monte–Carlo simulations with classical potentials. Predicted photoelectron spectra of aqueous alkali halide solutions are stable with respect to cluster size, basis set and self–energy approximations, and the sampling of solvent configurations. Dyson orbitals reveal a fundamental difference in electronic structure between fluoride and other halide solutions. Strong hydrogen bonding in the former case is responsible for delocalization of Dyson orbitals over many solvent molecules near the ionization threshold and for the dispersion of the fluoride contribution to the density of states over the inner–valence region of the spectrum. For other halides, Dyson orbitals near the ionization threshold are more localized on the anionic center.

This work is supported by the National Science Foundation.