Propagator Theory of Correlation–Bound Anions and Their Dyson Orbitals

J. V. Ortiz

Department of Chemistry and Biochemistry
Auburn University
Auburn, Alabama 36849-5312

2018 Sanibel Symposium

Abstract

Recent developments in *ab initio* electron propagator theory provide efficient, accurate and versatile means to calculating electron binding energies of molecules and ions and to interpreting these results with one–electron concepts that emerge from a correlated, many–body formalism. Systematic procedures for generating electron propagators of any order in the Møller–Plesset fluctuation potential and for saturation of basis–set effects through explicit–correlation operator manifolds hold considerable promise for predictions of high precision. Repartitioning of the operator space employed in the Dyson equation enables perturbative improvements to generalized orbital energies that follow from a variety of reference Slater determinants. Numerical tests of the P3+, NR2 and BDT self–energy approximations demonstrate their computational and conceptual advantages in the pursuit of novel chemistry. In addition to providing accurate predictions on various spectral probes of valence–bound anions, such as novel kinds of super–halides, these methods also generate precise data on species that would not be bound except for strong electron correlation, including double-Rydberg anions, solvated electron precursors and diffuse and valence excited states of fullerides.