A New Generation of Electron–Propagator Self–Energies for Calculations on Anions: Benchmarks and Applications to Nucleotides

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A new generation of self-energy approximations in *ab initio* electron propagator theory for the calculation of electron detachment energies of molecular anions has been derived from an intermediately normalized, Her- mitized super–operator metric. These methods and widely used antecedents such as the outer valence Green's function and the approximately renormal- ized partial third order method are tested with respect to a data set of 55 vertical electron detachment energies of anions. Several modifications of the diagonal second-order self-energy, a version of G_0W_0 theory based on Tamm-Dancoff excitations and several older, non–diagonal self-energies such as ADC(3), NR2 and BD–T1 also are included in the tests. All considered methods employ canonical Hartree–Fock orbitals. No adjustable or empir- ical parameters appear. Mean absolute errors of 0.2 and 0.1 eV have been realized respectively by self–energies with cubic (OV^2) or quintic (O^2V^3 or OV^4) arithmetic scaling. The new methods with diagonal self–energy ma- trices are the foundation of a composite procedure for estimating basis–set effects. This model produces accurate predictions and clear interpretations based on Dyson orbitals for the photoelectron spectra of the nucleotide an- ions found in DNA.

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