A New Generation of Diagonal and Non–diagonal Self-Energies for the Calculation of Electron Removal Energies

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A new generation of diagonal and non–diagonal self-energy approximations in *ab initio* electron propagator theory for the calculation of electron removal energies of molecules and molecular ions has been derived from an intermediately normalized, Hermitized super–operator metric.

These methods and widely used antecedents such as the outer valence Green's function and the approximately renormalized partial third order method are tested with respect to a data set of vertical ionization energies generated with a valence, triple–ζ, correlation–consistent basis set and a converged series of many–body calculations whose accuracy approaches that of full configuration interaction. Another test employs ΔCCSD(T) results for the GW100set. 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 also are included in the tests. All new methods employ canonical Hartree –Fock orbitals. No adjustable or empirical parameters appear. A hierarchy of methods with optimal accuracy for a given level of computational efficiency is established. Several widely used diagonal self –energy methods are rendered obsolete by the new hierarchy.