New–Generation Electron–Propagator Methods for Calculations of Molecular Electron–Binding Energies and Dyson Orbitals

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A new generation of *ab initio* self–energy approximations has surpassed its antecedents with respect to accuracy, efficiency and interpretability. Nu- merical tests on several data bases of electron binding energies have estab- lished the superiority of the new methods for closed–shell initial states. An opposite–spin simplification of the diagonal second–order self–energy yields mean absolute errors (MAEs) of 0.2 eV with a cubic arithmetic bottle- neck. Approximately renormalized extensions derived from an intermedi- ately normalized, Hermitized super–operator metric obtain MAEs of 0.1 eV with fifth–power bottlenecks. Explicitly renormalized diagonal self–energies produce slight improvements with more fifth–power matrix multiplications. Non–diagonal, renormalized self-energies realize minor reductions in MAEs and introduce non–iterative, sixth–power contractions. All new–generation methods employ canonical Hartree–Fock orbitals. No adjustable or empiri- cal parameters appear.

Applications to organic photovoltaic molecules with a composite model produce MAEs near 0.05 eV. A study of nucleotide anions predicts the verti- cal electron detachment energy of guanosine to within 0.05 eV of experiment and explains trends in the localization of Dyson orbitals.