Electron-Propagator Self-Energies Versus Improved GW100 Vertical Ionization Energies

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Abstract

Ab initio, electron-propagator (EP) methods that are free of adjustable parameters in their self-energy formulae and in the generation of their orbital bases have been applied to the calculation of the lowest vertical ionization energies (VIEs) of the GW100 set. An improved set of standard results accompanied by irreducible representation assignments has been produced indirectly with coupled-cluster singles-and-doubles plus perturbative triples, i.e., CCSD(T), total-energy differences at initial-state geometries re-optimized (in 28 cases) with the largest applicable point groups. The best compromises of accuracy and efficiency belong to a new generation of electron-propagator self-energies, several members of which may be derived from an intermediately normalized, Hermitized super-operator metric. The following diagonal self-energy methods are optimal: opposite-spin non-Dyson second order (os-nD-D2), approximately renormalized partial third order (P3+), approximately renormalized quasiparticle third order (Q3+), and non-Dyson approximately renormalized linear third order version B (nD-L3+B). Their mean absolute errors (MAEs) in eV and arithmetic scaling factors expressed in terms of occupied (O) and virtual (V) orbital dimensions are respectively: (0.18, OV^2), (0.14, O^2V^3), (0.15, O^2V^3), (0.11, OV^4). The 0.06 eV MAE for the non-diagonal, sixth-power (O^2V^4) Brueckner-Doubles, Triple-Field-Operator (BD-T1) EP method is exceeded by the 0.10 eV MAE with respect to experiment inherent in seventh-power, ΔCCSD(T) calculations and indicates that BD-T1 may serve as a direct, spin-symmetry-conserving alternative in the generation of standard results for VIEs of larger, closed-shell molecules.