Explicitly correlated second-order Green's Function (GF2-F12) for ionization energies

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Explicitly correlated second-order Green's function (GF2-F12)[1] is presented and applied to polycyclic aromatic hydrocarbons (PAHs), oligothiophene, and porphyrins. GF2 suffers from slow convergence of orbital expansions as in the ordinary post Hartree–Fock methods in *ab initio* theory, albeit the method is capable of providing quantitatively accurate ionization energies (IE) near the complete basis set limit for conjugated π-systems. This feature is significantly mitigated by introducing F12 terms of explicitly correlated electronic structure theory. It is demonstrated that GF2-F12 presents accurate IE with augmented triple-zeta quality of basis sets. The errors from experimental results are typically less than 0.15 eV for PAHs.

[1] Y.-y. Ohnishi, S. Ten-no, *J. Comput. Chem.*, **37**, 2447-2453 (2016).