A non-empirical improvement of PBE and its hybrid PBE0

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A non-empirical re-parameterization of the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional and of the related PBE hybrid (PBE0) follows from imposing the constraint that the functional be one-electron self-interaction free for the hydrogen atom. The new parameterization shifts the μ parameter upward with respect to PBE, (0.27583 vs. 0.21951), whereas the PBEsol parameterization for solids shifts μ downward to the gradient expansion value, $10/81 \approx 0.12346$. We report the usual tests of heats of formation, ionization potentials, electron and proton affinities, binding energies of weakly interacting systems, hydrogen and non-hydrogen transfer reaction barrier heights, bond distances and harmonic frequencies, for well-known test sets. The re-parameterized PBE GGA, called PBEmol, gives a substantial improvement over the original PBE in predicted heats of formation, while retaining essentially the quality of the original PBE functional for description of the other properties. Results for the hybrids indicate that, although the PBE0 functional provides a rather good description of those properties, the predictions of the re-parameterized functional, PBEmolβ0, are, except in the case of the ionization potentials, modestly better. Also, the results for PBEmolβ0 are better than B3LYP, except for the case of the ionization potentials and the harmonic frequencies.