A density functional for core-valence correlation energy

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A density functional, $\varepsilon_{\text{CV-DFT}}(\rho_c, \rho_v)$, describing the core-valence correlation energy has been constructed as a linear combination of $\varepsilon_{\text{LYP}}^{\text{corr}}(\rho_c)$, $\varepsilon_{\text{VWN5}}^{\text{corr}}(\rho_c, \rho_v)$, $\varepsilon_{\text{PBE}}^{\text{corr}}(\rho_c, \rho_v)$, $\varepsilon_{\text{Slater}}^{\text{ex}}(\rho_c, \rho_v)$, $\varepsilon_{\text{HCTH}}^{\text{ex}}(\rho_c, \rho_v)$, $\varepsilon_{\text{HF}}^{\text{ex}}(\rho_c, \rho_v)$, and $\text{F}_{\text{CV-DFT}}(\text{N}_i, \text{Z}_i)$, a function of the nuclear charges. This functional, with 6 adjustable parameters, reproduces (±0.27 kcal/mol rms error) a benchmark set of 194 chemical energy changes including 9 electron affinities, 18 ionization potentials, and 167 total atomization energies covering the first- and second-rows of the periodic table. This is almost twice the rms error (±0.16 kcal/mol) obtained with CCSD(T)/MTsmall calculations, but less than half the rms error (±0.65 kcal/mol) obtained with MP2/GTlargeXP calculations, and somewhat smaller than the rms error (±0.39 kcal/mol) obtained with CCSD/MTsmall calculations. The largest positive and negative errors from $\varepsilon_{\text{CV-DFT}}(\rho_c, \rho_v)$ were 0.88 and −0.75 kcal/mol with the set of 194 core-valence energy changes ranging from +3.76 kcal/mol for the total atomization energy of propyne to −9.05 kcal/mol for the double ionization of Mg. Evaluation of the $\varepsilon_{\text{CV-DFT}}(\rho_c, \rho_v)$ functional requires less time than a single SCF iteration, and the accuracy is adequate for any model chemistry based on the CCSD(T) level of theory.