Minimally empirical double hybrids: A status update

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ABSTRACT

Minimally empirical double hybrid DFT (see [1] for a review) has emerged as an middle road between WFT and hybrid DFT that achieves accuracy near WFT at a computational cost not much greater than conventional hybrid DFT (for small and medium molecules). "Minimal empiricism" eschews the extremes of both radically empirical "quasi-machine learning" on the one hand, and nonempirical purism on the other: adjustable parameters are used sparingly and only when statistically significant beyond any doubt. The first and most widely used such functional, revDSD-PBEP86 [2], was competitive with the best double hybrid thus far, but with one-third the number of adjustable parameters. Various avenues for further improvement have been explored, culminating in Refs.[3,4]. The RI-MP2 step dominates computational cost for large systems ($\gtrsim$100 nonhydrogen atoms), but here PNO-MP2-F12 approaches [5] offer a viable solution.

References

[1] Martin, J.M.L.; Santra, G. Empirical Double-Hybrid Density Functional Theory: A 'Third Way' in Between WFT and DFT. *Isr. J. Chem.* **2020**, *60*, 787-804.

[2] Santra, G.; Sylvetsky, N.; Martin, J.M.L. Minimally Empirical Double Hybrid Functionals Trained Against the GMTKN55 Database: revDSD-PBEP86-D4, revDOD-PBE-D4, and DOD-SCAN-D4, *J. Phys. Chem. A* **2019**, 123, 5129-5143

[3] Santra, G.; Semidalas, E.; Martin, J.M.L. Surprisingly Good Performance of XYG3 Family Functionals Using Scaled KS-MP3 Correlation. *J. Phys. Chem. Lett.* **2021,** *12*, 9368-9376.

[4] Becke, A.D. ; Santra, G.; Martin, J.M.L. A double-hybrid density functional based on good local physics with outstanding performance on the GMTKN55 database. *J. Chem. Phys.* **2023**, *158*, 151103.

[5] Mehta, N.; Martin, J.M.L. Reduced-scaling double hybrid DFT with rapid basis set convergence through localized pair natural orbital F12, *J. Phys. Chem. Lett.* **2022**, *13*, 9332-9338.