New 'low-cost' electronic structure methods for large systems

Stefan Grimme

Mulliken Center for Theoretical Chemistry, Clausius Institute for Physical and Theoretical Chemistry, University of Bonn, Beringstraße 4, 53115 Bonn, Germany

At the previous Sanibel meeting I introduced a new, special purpose tight-binding (TB) electronic Hamiltonian termed PTB[1] which is expressed in an accurate polarized valence double-zeta AO basis set (vDZP). The basis set has been specially optimized in molecular DFT calculations using standard ECPs for all elements up to radon[2]. The combination of the accurate wB97X(-V)[3] RSH functional with vDZP/ECP and an adjusted D4 dispersion correction defines a new member in our hierarchy of efficient composite electronic structure methods, termed wB97X-3c[2]. This basis set optimization concept is furthermore applied to a minimal set of AOs which - as a totally new ingredient - is made adaptive, i.e., radially different for symmetry distinct atoms in a molecule. The "breathing" of the AOs in the molecular environment is parameterized efficiently by on-the-fly computed effective atomic charges and coordination numbers. This so-called q-vSZP set[4] provides in typical DFT applications results of about or better than DZ quality. It forms the basis of our third-generation tight-binding model GP3-xTB which includes non-local Fock-exchange as well as other new, many-center Hamiltonian terms (e.g., atomic correction potentials, ACP). It aims at general purpose (GP) applicability in chemistry and more closely approaches DFT accuracy (actually wB97X-D4/TZ) than previous semi-empirical methods at only slightly increased computational cost (factor of 2-3 compared to GFN2-xTB). The talk describes key improvements of the underlying TB theory as well as extensive benchmarking on a wide range of standard thermochemistry sets.

[1] S. Grimme, M. Müller, A. Hansen, J. Chem. Phys., 158 (2023), 124111
[2] M. Müller, A. Hansen, S. Grimme, J. Chem. Phys. 158 (2023), 014103
[3] N. Mardirossian and M. Head-Gordon, Phys. Chem. Chem. Phys. 16 (2016), 9904
[4] M. Müller, A. Hansen, S. Grimme, J. Chem. Phys., in press.