

New tight-binding electronic structure methods

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All widely used semi-empirical quantum chemical methods like PM6, DFTB, or GFN-xTB are formulated in a (almost) minimal basis set of atomic orbitals, which limits the achievable accuracy for many important chemical properties. Recently, we proposed a new special purpose tight-binding (TB) electronic Hamiltonian termed PTB which is expressed in an accurate polarized valence double-zeta AO basis set (vDZP). The basis has been specially optimized in molecular DFT calculations using standard ECPs for all elements up to radon. The PTB method aims primarily at reproducing the one-particle density matrix of a DFT reference calculation with the wB97X-V range-separated hybrid density functional in exactly the same AO basis. It enables the computation of dipole moments and static polarizabilities with corresponding Cartesian derivatives for the simulation of IR and Raman vibrational spectra intensities. The PTB procedure is non-self-consistent employing only two matrix diagonalizations, includes new non-local potentials, as well as established parts from GFN-xTB and requires only simple overlap integrals as input. Compared to the wB97X-V/vDZP reference calculations, speedups of 3-4 orders of magnitude are achieved so that runs for molecules with 100-200 atoms are completed in a few seconds of computation time on standard desktop computers. The use of the PTB density in typical computational chemistry applications as well as for non-iterative DFT schemes or in extremely fast TB energy expressions is discussed.