Semiempirical MO-Theory for Large Systems

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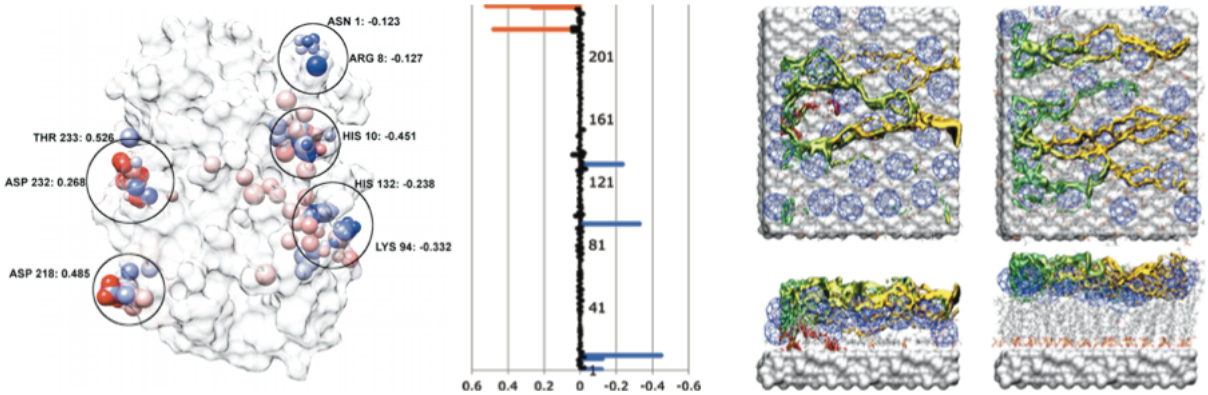

We present a comparison of conventional semiempirical wavefunction based MNDO-like methods and approximate linear-scaling methods for large molecules. Until recently, linear-scaling methods such as divide and conquer (D&C) [1] or localized-molecular-orbital (LMO) [2] techniques were essential for the treatment of large systems by means of semiempirical MO theory. However, conventional full SCF calculations based on a massively parallel code (EMPIRE [3]) now allow very large systems to be treated without local approximations. The comparison revealed a very slow SCF convergence for gas-phase calculations on zwitterionic proteins using a full SCF routine, whereas LMO SCF converges rapidly. Further comparative calculations with both techniques showed that the very slow inductive charge-transfer process that made the conventional SCF calculations so slow to converge is prevented in the LMO-SCF scheme. Therefore, the LMO procedure can lead to artificially over-polarized wavefunctions in gas-phase calculations. Example molecules have been constructed to demonstrate this behavior.[4] Further, recent applications of semiempirical MO-theory in the field of Self-Assembled Monolayer Field-Effect Transistors (SAMFETs) are presented.[5–7]

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