The Quest for Accurate Semiempirical Methods

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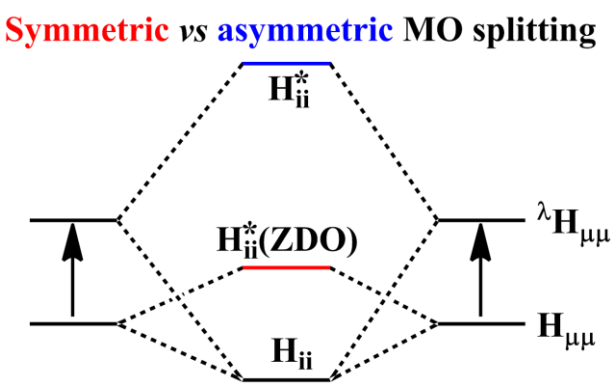
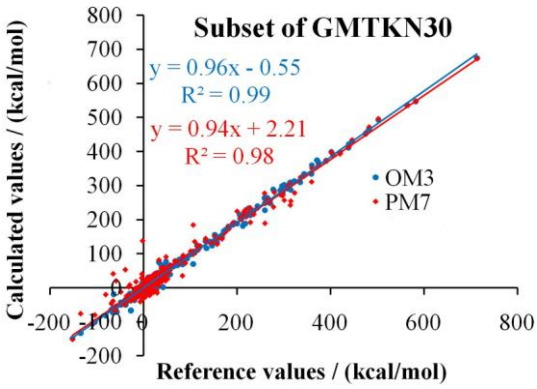
Semiempirical quantum chemical (SQC) methods are computationally efficient techniques for calculating electronic structure properties of very large systems or for a huge number of smaller systems, for which other quantum chemical methods would not be computationally feasible. Over the last decades SQC methods were systematically improved mainly using two distinct approaches, both starting from the MNDO model.

The first one concentrated on enhancements within the MNDO framework, primarily by modifying the core-core repulsion function and increasing the number of reference data used to fit the SQC parameters for more and more elements. The most widely used methods of this class are (in chronological order) AM1, PM3, MNDO/d, PDDG-MNDO and PDDG-PM3, AM1*, RM1, PM6, and PM7. [1]

The second methodology focused on introducing explicit corrections to the MNDO model to account for the non-orthogonality of the basis set. Corresponding orthogonalization-corrected methods (OM*x*) OM1, OM2 and OM3 appear to be a practical tool for many applications, especially in excited-state studies. [1] Early excited-state benchmark studies revealed the higher accuracy of OM*x* methods compared to traditional SQC techniques, which is attributed to the asymmetric MO splitting in OM*x* methods. [1] Moreover, OM*x* methods were shown to be robust techniques for calculating ground-state properties with accuracy often similar to that of DFT. [2]





Here we significantly extend previous ground-state benchmark studies [1, 2] to test more SQC methods on huge collections of high-quality reference data. Our studies confirm the high robustness of OM*x* methods in comparison with other SQC methods and provide guidelines for choosing an appropriate SQC method for the problem at hand. [3]

We also benchmarked various explicit dispersion corrections to SQC methods on high-quality benchmark sets and determined the best combinations of SQC method and dispersion correction for different types of noncovalent interactions. [3]

Finally we outline current developments for improving the accuracy of SQC methods by using both traditional techniques and novel approaches based on machine learning.

[1] W. Thiel, *WIREs Comput. Mol. Sci.* **2014**, *4*, 145-157.
[2] M. Korth, W. Thiel, *J. Chem. Theory Comput.* **2011**, *7*, 2929-2936.
[3] P. O. Dral, X. Wu, L. J. Spörkel, A. A. Nikiforov, A. Koslowski, W. Thiel, *J. Chem. Theory Comput.*, to be submitted.