Semiempirical quantum chemistry: Methodology and dynamics

Walter Thiel
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim, Germany
E-mail: thiel@kofo.mpg.de

Semiempirical quantum-chemical methods are well-established tools for computational studies of large molecules [1]. Methods with explicit orthogonalization corrections (OM1, OM2, OM3) offer better overall accuracy in standard statistical evaluations of ground-state properties as well as qualitative improvements for hydrogen bonding and conformational properties [2,3]. OMx-based studies of electronically excited states employ a general implementation of the GUGACI approach in a semiempirical framework which provides analytic gradients and nonadiabatic couplings. Comparisons with high-level ab initio benchmark data show that OMx/MRCI methods describe electronically excited states reasonably well [4]. They can thus be used in mixed quantum-classical dynamics to investigate fast nonradiative relaxation processes after photoexcitation [1,5].

The lecture will address the theoretical background of the OMx methods including the ZDO approximation and report on recent comprehensive benchmarks. Thereafter it will cover unpublished work that has led to the development of the ODM2 method with integrated orthogonalization and dispersion corrections. In addition, it will present selected OM2/MRCI studies of surface-hopping excited-state dynamics; recent examples include simulations on light-driven rotary molecular motors [6], GFP chromophores [7], arylazopyrazole photoswitches [8], and tetraphenylethene derivatives [9].

[1] W. Thiel, *WIREs Comp. Mol. Sci.* **4**, 145-157 (2014).
[2] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Weber, R. Steiger, M. Scholten, W. Thiel, *J. Chem. Theory Comput*. **12**, 1082-1097 (2016).
[3] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Thiel, *J. Chem. Theory Comput*. **12**, 1097-1120 (2016).
[4] D. Tuna, Y. Lu, A. Koslowski, W. Thiel, *J. Chem. Theory Comput.* **12**, 4400-4422 (2016).
[5] L. Spörkel, W. Thiel, *J. Chem. Phys.* **144**, 194108 (2016).
[6] A. Nikiforov, J. A. Gamez, W. Thiel, M. Filatov, *J. Chem. Phys. Lett*. **7**, 105-110 (2016).
[7] X.-Y. Liu, X.-P. Chang, S.-H. Xia, G. Cui, W. Thiel, *J. Chem. Theory Comput*. **12**, 753-764 (2016).
[8] Y.-T. Wang, X.-Y. Liu, G. Cui, W.-H. Fang, W. Thiel, *Angew. Chem. Int. Ed*. **55**, 14009-14013 (2016).
[9] Y.-J. Gao, X.-P. Chang, X.-Y. Liu, Q.-S. Li, G. Cui, W. Thiel, *J. Phys. Chem. A* **121**, 2572-2579 (2017).