RECENT ADVANCES IN THE ACCURATE CALCULATION OF NMR PARAMETERS

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Highly accurate calculations of NMR parameters are still a challenge to quantum chemistry. For nuclear magnetic shielding constants GIAO-CCSD(T) and for indirect spin-spin coupling constants CCSD calculations have been very successful. However, further theoretical developments are needed to validate the accuracy of these approaches, to improve upon the currently available results, and to increase the range of applicability of the available methods to larger molecular systems. To cope with these challenges, the following advances in the calculation of NMR parameters are presented:

- Implementation of the GIAO-CCSDT model for the computation of NMR shielding constants at the full coupled-cluster singles, doubles, and triples (CCSDT) level. GIAO-CCSDT calculations allow for the first time a rigorous analysis of the performance of schemes for the approximate treatment of triple excitations such as, for example, GIAO-CCSD(T) or the GIAO-CCSDT-n (n=1-3) approaches.

- Consideration of zero-point vibrational effects in the calculation of NMR shielding constants via a perturbational approach. The importance of vibrational corrections is discussed for absolute shieldings as well as for relative ^{13}C and ^{19}F NMR chemical shifts.

- Treatment of electron correlation effects on nuclear magnetic shieldings within local correlation schemes, thus offering in the long run the possibility to treat larger molecular systems in a routine manner. A first preliminary implementation of the GIAO-LMP2 (LMP2 = local MP2) is presented together with first results which document the suitability of such an approach.

- Triple excitation effects are for the first time investigated in coupled-cluster calculations of indirect spin-spin coupling constants. Comparison with CCSDT results leads to recommendations for the best strategy concerning the approximate inclusion of triple excitations in coupled-cluster calculations of spin-spin coupling constants.