

Linear-scaling calculation of NMR chemical shifts

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- A new method for the calculation of NMR chemical shieldings has recently been introduced by Kussmann and Ochsenfeld in 2004 (Angew. Chemie Int. Ed. **43**, 4485-4589 (2004)), which allows for the first time the computation of chemical shifts for 1000 and more atoms at the HF and DFT level (with no need for molecular symmetry). This overcomes the restriction of conventional NMR calculation methods to systems in the order of 100 atoms. The treatment of large molecules becomes possible by the reduction of the conventional cubic increase of the computational effort with molecular size to linear. The new method opens up new possibilities for the assignment of observed NMR spectra both in solution and solid state, which is illustrated as well by the cover page of the Angew. Chemie [1]. In Ref. [1] as well two first applications are presented for molecular tweezer systems converging both solution and solid state NMR spectra with respect to the number of surrounding molecules.
- The implementation of the new method [1] in Q-Chem at the HF- and KS-DFT-level is based on the use of gauge-including atomic orbitals (GIAO). For linear scaling integral contractions within the new method [1] LinK [2,3] and CFMM [4,5] schemes have been extended. For an overall linear scaling for large molecular systems with a non-vanishing HOMO-LUMO gap, not only integral contractions are done in a linear-scaling fashion, but as well the perturbed SCF equations are solved linearly by the D-CPSCF (density matrix-based coupled perturbed SCF) method described in Ref.[1]
- The current implementation is limited to basis sets with a maximum angular momentum of 2 (d-functions).

References:

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