Linear- and Sub-Linear Scaling Quantum-Chemical Methods

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The usefulness of the Laplace transformation for the formulation of linear-scaling methods is discussed for both response theories at Hartree-Fock (HF) and Density-Functional Theory (DFT) levels [1], and for the calculation of energies and energy gradients at the Møller-Plesset (MP2) level [2-4]. The transformation allows to entirely avoid the delocalized, canonical molecular orbital (MO) representation, which is crucial for the formulation of linear-scaling methods. In this way, only density or pseudo-density matrix-based quantities enter the formulations, so that sparsity can be exploited for electronically local molecular systems and linear scaling is attained. The largest system computed at the MP2 level is an RNA system comprising 1664 atoms and 19 182 basis functions [5].

Furthermore, we introduce a sub-linear scaling NMR method [6], that allows to compute NMR shieldings for selected nuclei only. This has important implications not only for the study of large molecules, but also for the simulation of solvent effects and molecular dynamics, since often just a few shieldings are of interest. Our theory relies on two major aspects both necessary to provide a sublinear scaling behavior: First, an alternative expression for the shielding tensor is derived, which involves the response density matrix with respect to the nuclear magnetic moment instead of the response to the external magnetic field. Second, as unphysical long-range contributions occur within the description of distributed gauge origin methods that do not influence the final expectation value, we present a reformulation suitable for truncation, so that an early onset of the sublinear-scaling behavior can be achieved. Applications to molecular systems with more than 1000 atoms will be shown.

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