Linear- and sublinear-scaling Møller-Plesset (MP2) and symmetry-adapted perturbation theory (SAPT)

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Linear-scaling methods for both energy calculations at the MP2 level and the direct calculation of intermolecular interactions at the SAPT level are presented using a combination of distance-including integral estimates, linear-scaling integral contractions, and fully AO-based Laplace techniques that allow to access molecules with more than 1000 atoms [1,2]. The key feature of our linear-scaling correlation methods are distance-including two-electron integral estimates that allow to exploit the $1/R^4$ or even $1/R^6$ decay behavior of transformed integrals. Our two-electron integral estimates combine ideas of multipole-expansions and regular Schwarz bounds into so-called QQR integral estimates that are both tight and simple estimates [3] generally applicable in quantum-chemical methods. The largest system calculated so far for determining, e.g., SOS-MP2 energies is a DNA-repair complex comprising 2025 atoms and 20 371 basis functions accessible on simple workstation clusters [1]. To allow for the use of larger basis sets, we employ a combination of the resolution-of-the-identity (RI) for two-electron integrals and a Cholesky-decomposition of pseudo-density matrices within AO-based formulations (Cholesky-decomposed density MP2: CDD-MP2) [4-5]. Besides energy calculations, we present a reformulation of nuclei-selected NMR chemical shieldings at the MP2 level that opens the way to reduce the conventional MO-based $\mathcal{O}(\mathrm{M}^5)$ scaling to $\mathcal{O}(\mathrm{M}^0)$ [6].

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