Numerical solution of the Hartree-Fock equation by the tensor-structured methods

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Abstract

The classical Hartree-Fock equation is one of the basic *ab initio* models in electronic structure calculations. Traditionally, its solution is based on a rigorous analytical precomputation of the arising convolution type integrals in $\mathbb{R}^3$ which requires the naturally separable basis.
We propose the novel grid-based tensor-structured methods for the numerical solution of the Hartree-Fock equation, which can be used as well in other models in quantum chemistry. These methods include efficient algorithms for the separable representation of the discretized functions and integral operators in $\mathbb{R}^3$ using the canonical, Tucker and mixed tensor formats and the corresponding fast tensor operations. The core of our "black-box" solver is the rank-structured computation of the nonlinear Hartree and the (nonlocal) exchange parts of the Fock operator in $\mathbb{R}^3$, discretized on a sequence of $n \times n \times n$ Cartesian grids. The arising $3D$ and $6D$ convolutions with the Newton kernel are substituted by $1D$ algebraic operations implemented with $O(n \log n)$ complexity. Note that in terms of usual estimation by volume size $N_{vol} = n^3$, the tensor-structured operations are of sublinear complexity, $O(N_{vol}^{1/3})$.
The robust multigrid canonical-to-Tucker rank reduction algorithm for $3D$ tensors in 1D complexity enables usage of fine Cartesian grids up to $n^3 \approx 10^{12}$. This yields high resolution of the involved computational quantities and allows arbitrary location of atoms in a molecule as in the traditional mesh-free analytical-based solution of the Hartree-Fock equation. Numerical results for several moderate size volumetric molecules demonstrate efficiency of the tensor-structured methods in electronic structure calculations.

References

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