Accurate Solution of the Hartree-Fock Equation by the Tensor-structured Methods

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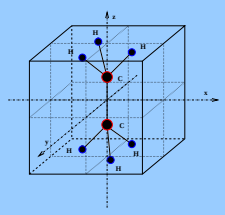


Two-level Tucker-canonical tensor format in $\mathbb{R}^d$

We approximate the *d-th order tensors* (function of discrete variables)

$$A = [a_{i_1 \dots i_d}] \in \mathbb{R}^{n^d},\ i_\ell = 1, \dots, n,\ \ell = 1, \dots, d,\ n \in \mathbb{N}; \quad S(A) = n^d,$$

by the short-term sum of rank-1 tensors.

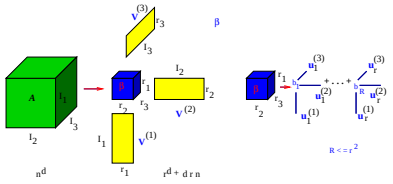
Canonical model: using a sum of normalized rank-1 tensors

$$A_{(R)} = \sum_{k=1}^{R} c_k u_k^{(1)} \otimes \dots \otimes u_k^{(d)} \approx A.$$

Tucker model: using orthonormalized set $\{V_{k_\ell}^{(\ell)} \in \mathbb{R}^n,\ k_\ell = 1, \dots, r\}$,

$$A_{(\mathbf{r})} = \sum_{k_1=1}^{r} \dots \sum_{k_d=1}^{r} b_{k_1 \dots k_d} V_{k_1}^{(1)} \otimes \dots \otimes V_{k_d}^{(d)} \approx A.$$

Mixed format:



Tensor Approximation of the Hartree-Fock equation

The Hartree-Fock equation for the N-electron system is a self-consistent eigenvalue problem (EVP)

$$\left(-\frac{\Delta}{2} + V_{nucl} + V_H\right)\varphi_i(\mathbf{x}) - \int_{\mathbb{R}^3} \frac{\tau(\mathbf{x},\mathbf{y})\varphi_i(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} = \lambda_i \varphi_i(\mathbf{x})$$

for $i = 1, \dots, N/2$, where N is the number of electrons in a molecule.

Computation of the Hartree potential.

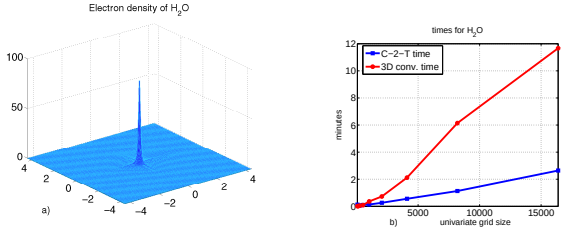
The Hartree potential

$$V_H = \int_{\mathbb{R}^3} \frac{\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \equiv \rho * \frac{1}{|\mathbf{x}|},\ \rho(\mathbf{x}) = 2\tau(\mathbf{x},\mathbf{x}),\ \tau(\mathbf{x},\mathbf{y}) = \sum_{i=1}^{N/2} \varphi_i(\mathbf{x})\varphi_i(\mathbf{y}).$$

V_H is computed by the tensor product convolution.
Electron density ρ is represented by the rank-R_{ρ_r} canonical tensor F.
Newton potential $\frac{1}{|x|}$ is approximated by the rank-R_N ($R_N \sim 20 \div 30$) canonical tensor G obtained by the optimised *sinc*-quadratures.

$$V_H \approx F * G = \sum_{k=1}^{R_N} \sum_{m=1}^{R_{\rho_r}} c_k b_m \left(u_1^k * v_1^m\right) \otimes \left(u_2^k * v_2^m\right) \otimes \left(u_3^k * v_3^m\right)$$

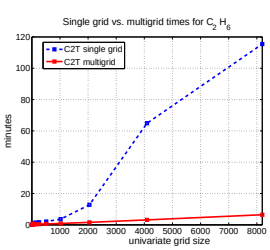
which leads to the cost $O(RR_1 n \log n) \ll O(n^3 \log n)$, where the latter corresponds to 3D FFT.
The initial large rank $R_\rho \sim R_0^2 \sim 10^4$ is reduced to $R_{\rho_r} \sim 10^2$ by the **Multigrid Accelerated canonical-to-Tucker algorithm (C2T)**.

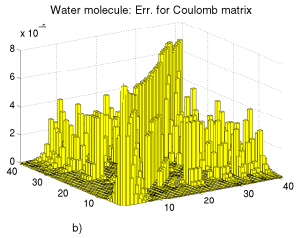


Electron density of the water molecule (left) and the times for computation of the C2T and 3D convolution (right), up to the grid size 16384^3 (in Matlab).

Computation of the Coloumb matrix.

$J_{km} := \int_{\mathbb{R}^3} g_k(\mathbf{x}) g_m(\mathbf{x}) V_H(\mathbf{x}) d\mathbf{x}, \quad k,m = 1, \dots, R_0,$
where $\{g_k\}$ represents the GTO basis set.

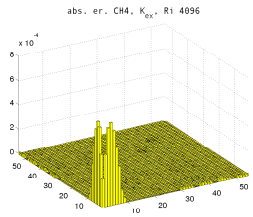


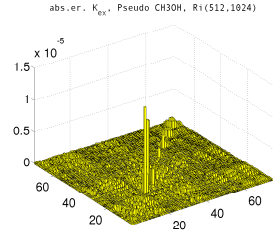


MG versus unigrid C2T times and the abs. error for the Coulomb matrix of H_2O.

Computation of the Exchange matrix.

$$\{K_{ex}\}_{k,m} := -\frac{1}{2}\int_{\mathbb{R}^3} g_k(\mathbf{x}) \frac{\tau(\mathbf{x},\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} g_m(\mathbf{y}) d\mathbf{x} d\mathbf{y}, \quad k,m = 1, \dots R_0$$

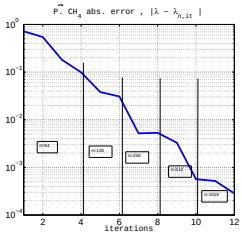


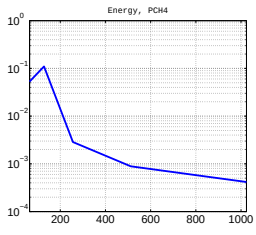


Abs. error for K_{ex} of CH_4 ($\sim 10^{-4}$) and the pseudopotential of CH_3OH ($\sim 10^{-5}$).

Iterative solution of the EVP in tensor format

Discrete Hartree Fock equation in GTO basis with the Fock matrix $F = H_0 + J(\rho(x)) - K_{ex}(\tau(x,y))$.
Our discrete version of the SCF method is based on:
(A) Initial guess $J = 0$, $K = 0$.
(B) Computation on a sequence of refined grids $n = n_0, 2n_0, \dots, 2^p n_0$.
(C) Solving EVP $[H_0 + J(\rho_m(x_n)) - K_{ex}(\tau_m(x_n, y_n))]\phi_{i,m} = \lambda_{i,m}\phi_{i,m}$
(D) Fast update of $J(\rho(x_n))$ and $K_{ex}(\tau(x_n, y_n))$ by computations in





Convergence of the eigenvalues in the EVP (left) w.r.t. iterations and of the E_{HF} energy w.r.t the univariate grid size of the EVP (right).

$E_{HF} = 2\sum_{i=1}^{N/2} \lambda_i - \sum_{i=1}^{N/2} \left(\tilde{J}_i - \tilde{K}_i\right),\ \tilde{J}_i = (\psi_i, V_H\psi_i)_{L^2}, \tilde{K}_i = (\psi_i, \mathcal{V}_{ex}\psi_i)_{L^2}$.

References

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Group Prof. W. Hackbusch