Numerical Solution of the Hartree-Fock Equation by the Tensor-Structured Methods

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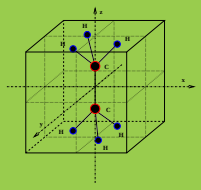


Tensor-structured formats

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

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

by the sum of rank-1 tensors.

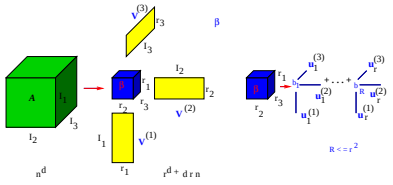
Canonical model: using a sum of normalized rank-1 tensors

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

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

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

Mixed format: Tucker model with canonical core $[\beta_{\mathbf{k}}]$



Numerical Solution of the Hartree-Fock Equation

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

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

Grid-based computation of the Hartree potential.

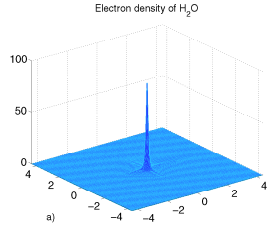
$$V_H = \int_{\mathbb{R}^3} \frac{\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \equiv \rho * \frac{1}{|\mathbf{x}|},\ \rho(\mathbf{x}) = 2\tau(\mathbf{x},\mathbf{x}),\ \tau(\mathbf{x},\mathbf{y}) = \sum_{i=1}^{N/2} \varphi_i(\mathbf{x})\varphi_i(\mathbf{y}).$$

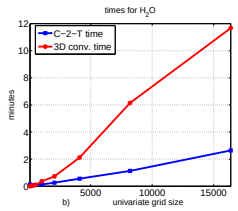
Electron density ρ is represented by the rank-R_ρ canonical tensor F. Newton potential $\frac{1}{|x|}$ is approximated by the rank-R_N ($R_N \sim 20 \div 30$) canonical tensor G obtained by the optimised *sinc*-quadratures.

$$V_H \approx F * G = \sum_{k=1}^{R_N} \sum_{m=1}^{R_\rho} c_k b_m \left(u_k^{(1)} * v_m^{(1)}\right) \otimes \left(u_k^{(2)} * v_m^{(2)}\right) \otimes \left(u_k^{(3)} * v_m^{(3)}\right),$$

with the cost $O(R_N R_\rho n \log n) \ll O(n^3 \log n)$, (vs. 3D FFT).

The initial large rank $R_{\rho_0} \sim R_0^2 \sim 10^4$ is reduced to $R_\rho \sim 10^2$ by the **Multigrid Accelerated canonical-to-Tucker algorithm (C2T).**





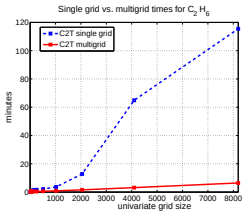
ρ for H_2O (left) and times for C2T and 3D convolution (right), grid size 16384^3. All computations in MATLAB.

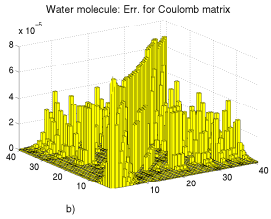
$(C * C)$ 3D convolution vs. 3D FFT (sec).

n^3	128^3	256^3	512^3	1024^3	2048^3	4096^3	16384^3
FFT_3	4.3	55.4	582.8	~ 6000	–	–	~ 2 years
$C * C$	0.2	0.9	1.5	8.8	20.0	61.0	299.2
C2T	4.2	4.7	5.6	6.9	10.9	20.0	86.0

The Coloumb matrix.

$J_{km} := \int_{\mathbb{R}^3} \overline{g}_k(\mathbf{x})\overline{g}_m(\mathbf{x}) V_H(\mathbf{x}) d\mathbf{x}, \quad k,m = 1, \dots, R_0,$
where $\{\overline{g}_k\}$ are grid-based GTOs.

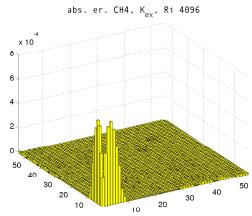


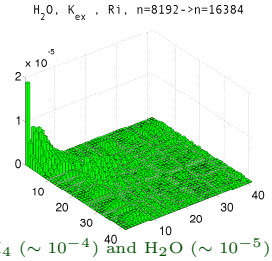


Times for MG versus unigrid C2T transform and the abs. error ($\sim 10^{-5}$) for the Coulomb matrix of H_2O.

Grid-based computation of the Exchange matrix.

$$K_{km} := \int_{\mathbb{R}^3} \overline{g}_k(\mathbf{x}) \frac{\tau(\mathbf{x},\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} \overline{g}_m(\mathbf{y}) d\mathbf{x} d\mathbf{y}, \quad k,m = 1, \dots R_0$$





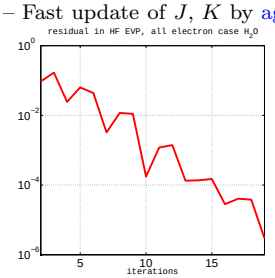
Abs. error in K for all electron case of CH_4 ($\sim 10^{-4}$) and H_2O ($\sim 10^{-5}$).

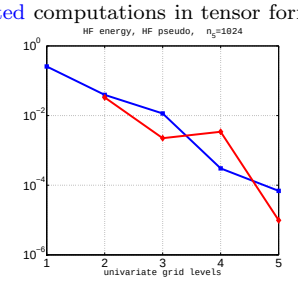
Multilevel "grey-box" 3D nonlinear EVP solver by the tensor-structured methods

The tensor-structured representation of all functions and operators on $n \times n \times n$ 3D Cartesian grid, based on $\varphi_i(x) \approx \sum_{k=1}^{R_0} c_{ki}\overline{g}_k(x)$, $i = 1, ..., N/2$. Find $C = \{c_{ki}\} = [C_1 ... C_{N/2}] \in \mathbb{R}^{R_0 \times N/2}$.

$$[H_0 + J(C) - K(C)]C_i = \lambda_i S C_i.$$

Core Hamiltonian matrix H_0 from MOLPRO.
– Initial guess $J = 0$, $K = 0$.
– Using a sequence of refined grids, $n = n_0, 2n_0, \dots, 2^p n_0$.
– Solving EVP $[H_0 + J(C) - K(C)]C_i = \lambda_i S C_i$.
– Fast update of J, K by agglomerated computations in tensor format.





Convergence of the EVP residual in iterations (left, for H_2O) and of E_{HF} energy vs. the level p of the n of $n \times n \times n$ Cartesian grid (pseudopot. of CH_4).

Main features of the tensor-structured methods:

- enable algebraic approximate separability of variables (at any step of computations),
- agglomerated tensor computations of V_H, J, K on $n \times n \times n$ 3D Cartesian grid scale linearly in the one-dimension grid size n,
- huge grids (16384^3, $h \approx 10^{-4}$ Å) provide high resolution, and hence, arbitrary location of atoms as in meshless methods,
- no need for analytic separability of basis functions, and for the analytical evaluation of two-electron integrals,
- may be gainfully applied in DFT.

http://personal-homepages.mis.mpg.de/vekh/