Tensor-structured solvers for the Hartree-Fock equation in a general basis

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Tensor-structured formats

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

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

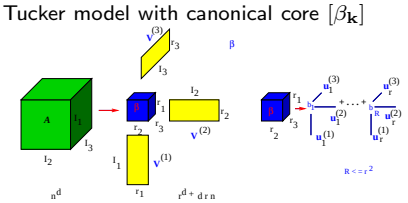
by the sum of rank-1 tensors in the canonical

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

and Tucker formats (with orthonormalized $v_{k_\ell}^{(\ell)}$, $k_\ell = 1, \dots, r$),

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

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



The Hartree-Fock equation for N-electron system,

$$\mathcal{F}\varphi_i(x) = \lambda_i \varphi_i(x), \quad i = 1, ..., N/2, \quad x \in \mathbb{R}^3,$$

with the Fock operator $\mathcal{F} := -\frac{1}{2}\Delta + V_c + V_H - \mathcal{K}$,

$$V_c(x) = -\sum_{\nu=1}^{M} \frac{Z_\nu}{\|x - a_\nu\|}, \quad Z_\nu > 0, \quad x, a_\nu \in \mathbb{R}^3,$$

$$V_H(x) := \int_{\mathbb{R}^3} \frac{\rho(y)}{\|x-y\|}\, dy, \quad \rho(y) = 2\sum_{i=1}^{N/2} (\varphi_i(y))^2,$$

$$(\mathcal{K}\varphi)(x) := \int_{\mathbb{R}^3} \frac{\tau(x,y)}{\|x-y\|} \varphi(y) dy, \quad \tau(x,y) = \sum_{i=1}^{N/2} \varphi_i(x)\varphi_i(y).$$

Solution: Galerkin discretization in a basis: $\{g_\mu\}_{1 \le \mu \le N_b}$,

$$\psi_i(x) = \sum_{\mu=1}^{N_b} c_{i\mu} g_\mu(x)$$

and DIIS iteration for computing $C = [c_{i\mu}] \in \mathbb{R}^{N_{orb} \times N_b}$,

$$F(D)C = SC\Lambda, \quad C^T S C = I_{N_b}, \quad F(C) = H + J(D) + K(D),$$

with the density matrix $D = 2CC^* \in \mathbb{R}^{N_b \times N_b}$, $\Lambda = diag(\lambda_1, ..., \lambda_{N_b})$, $1 \le \mu, \nu, \kappa, \lambda \le N_b$ and

$$J(D)_{\mu\nu} = \sum_{\kappa,\lambda=1}^{N_b} b_{\mu\nu,\kappa\lambda} D_{\kappa\lambda}, \quad K(D)_{\mu\nu} = -\frac{1}{2} \sum_{\kappa,\lambda=1}^{N_b} b_{\mu\lambda,\nu\kappa} D_{\kappa\lambda}.$$

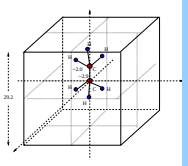
Standard approach: precalculation of two-electron integrals (TEI) in analytically separable basis (Gaussians):

$$b_{\mu\nu\kappa\lambda} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{g_\mu(x) g_\nu(x) g_\kappa(y) g_\lambda(y)}{\|x-y\|} dxdy.$$

Numerical challenges for large N: high accuracy, 3D/6D singular integrals, strong nonlinearity, nuclear cusps.

Tensor-structured calculus for the Fock operator

(3D integration in 1D complexity)



Computational box: $[-b, b]^3$, $b \approx 15$ Å
$n \times n \times n$ Cartesian grids, $n \sim 10^4 \div 10^6$,
$\phi_{\mathbf{i}}$ p.w. const/p.w. linear
$g_k(x) = \prod_{\ell=1}^{3} g_k^{(\ell)}(x_\ell) \mapsto G_k \in \mathbb{R}^{n \times n \times n}$,
$rank G_k = 1$

Tensor method I. (Compute J, K, "on the fly".)
Tensor rank reduction: multigrid C2T + T2C: $N_b^2/2 \approx 10^4 \Rightarrow R_\rho \sim 10^2$:

$$\rho \approx \Theta := \sum_{a=1}^{N_{orb}} \sum_{\kappa,\lambda=1}^{N_b} c_{\kappa a} c_{\lambda a} \mathbf{G}_\kappa \odot \mathbf{G}_\lambda \Rightarrow \Theta' = \sum_{m'=1}^{R_\rho} c_{m'} u_{m'}^{(1)} \otimes u_{m'}^{(2)} \otimes u_{m'}^{(3)},$$

$$V_H = \rho * \frac{1}{\|\cdot\|} \approx \Theta' * \mathbf{P}_N = \sum_{m'=1}^{R_\rho} \sum_{k=1}^{R_N} c_{m'} b_k \left(u_{m'}^{(1)} * v_k^{(1)}\right) \otimes \dots \otimes \left(u_{m'}^{(3)} * v_k^{(3)}\right)$$

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

$$J(C)_{\mu\nu} = \langle \overline{g}_\mu(x) \overline{g}_\nu(x), V_H(x) \rangle \approx \langle \mathbf{G}_\mu \odot \mathbf{G}_\nu, \Theta' * \mathbf{P}_N \rangle.$$

For 6D exchange operator K,

$$K(C)_{\mu,\nu} = \sum_{i=1}^{N/2} \langle \mathbf{G}_\mu \odot \left[\sum_{\kappa=1}^{N_b} c_{\kappa i} \mathbf{G}_\kappa\right], \left[\mathbf{G}_\nu \odot \sum_{\lambda=1}^{N_b} c_{\lambda i} \mathbf{G}_\lambda\right] * \mathbf{P}_N \rangle.$$

3D Laplacian in Galerkin basis (discretized by p.w. linear b.f.) is approximated by

$$\int_{\mathbb{R}^3} \nabla g_\mu \cdot \nabla g_\nu dx \approx a_{\mu\nu} = \langle A_3 \mathbf{G}_\mu, \mathbf{G}_\nu \rangle,$$

$$A_3 := A^{(1)} \otimes S^{(2)} \otimes S^{(3)} + S^{(1)} \otimes A^{(2)} \otimes S^{(3)} + S^{(1)} \otimes S^{(2)} \otimes A^{(3)}.$$

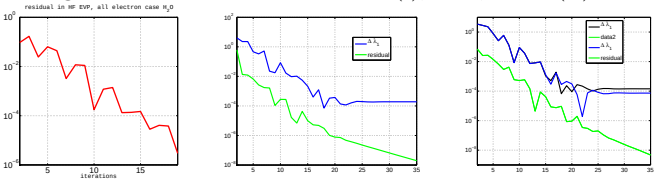
using 3D Cartesian grids with the max. number of entries 131072^3.
The nuclear potential: $\mathbf{P}_c = \sum_{m=1}^{M} Z_m \mathbf{P}_{N,m}$,

$$\overline{v}_{\mu\nu} = \int_{\mathbb{R}^3} V_c(x) \overline{g}_\mu(x) \overline{g}_\nu(x) dx \approx \langle \mathbf{G}_\mu \odot \mathbf{G}_\nu, \mathbf{P}_c \rangle.$$

Tensor method II. Compute factorized tensor TEI: $b_{\mu\nu\kappa\lambda} \cong \langle \mathbf{G}_\mu \odot \mathbf{G}_\nu, \mathbf{P}_N * (\mathbf{G}_\kappa \odot \mathbf{G}_\lambda) \rangle_{n^{\otimes 3}}$, using tensors $\mathbf{G} = \mathbf{G}_\mu \odot \mathbf{G}_\nu \in \mathbb{R}^{N_b \times N_b \times n^{\otimes 3}}$ and $\mathbf{H} = \mathbf{P}_{\mathcal{N}} * (\mathbf{G}_\kappa \odot \mathbf{G}_\lambda) \in \mathbb{R}^{R_N \times N_b \times N_b \times n^{\otimes 3}}$.

Compute Cholesky decomposition of $B := mat(\mathbf{B}) = [b_{\mu\nu,\kappa\lambda}] \mapsto LL^T$.
$J = BD \approx L(L^T D)$, $K = perm(\mathbf{B})D$, compexity $(O(N_{orb} N_b^2)$.

Convergence of EVP for molecules H_2O (I), NH_3, H_2O_2 (II)



Main features of the tensor-structured methods:

-enable algebr. approx. separability of variables at any step of computations,
-agglomerated "black box" tensor computations of V_H, J, K, H on 3D Cartesian grids in 1D complexity,
-3D integration is substituted by 1D Hadamard products, convolutions and scalar products.
-huge grids (16384^3, $h \approx 10^{-4}$ Å) provide high resolution,
-no need for analytic separability of basis functions.

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