Tensor numerical methods in 3D electronic structure calculations

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Outline of the talk

1. Tensor-structured methods in $\mathbb{R}^d$
   - Basic rank-structured formats
   - Tensor product operations
   - Why Tucker was important
   - Canonical to Tucker tensor approximation
2. Start of tensor-structured numerical methods
   - The Hartree-Fock (HF) equation
   - 3D grid-based Hartree and exchamge potentials in 1D complexity
3. HF Solver by a standard but 3D grid-based scheme
   - 3D grid-based factorized TEI
   - Core Hamiltonian
   - "Ab-initio" black-box HF solver
4. Grid-based extended and periodic systems
   - Assembled tensor method for lattice sums of long-range potentials

Rank-structured representation of higher order tensors

$A = [a_{i_1 \dots i_d}] \in \mathbb{R}^{n_1 \times \dots \times n_d}, \quad \ell = 1, \dots, d,$
for $n_\ell = n, \quad N = n^d$ –"curse of dimensionality".

$\Rightarrow$ We need structured representation of tensors:
Tensor product of vectors $u^{(\ell)} = \{u^{(\ell)}_{i_\ell}\}_{i_\ell=1}^{n} \in \mathbb{R}^{I_\ell}$ forms the canonical rank-1 tensor

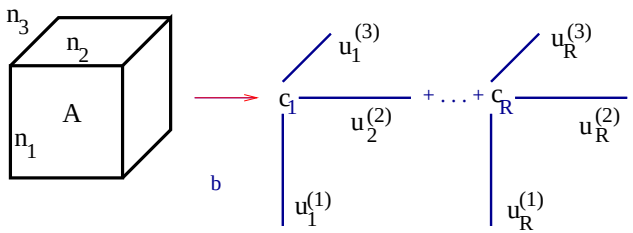
$$A_{(1)} = u^{(1)} \otimes \dots \otimes u^{(d)} \equiv [u_{\mathbf{i}}]_{\mathbf{i} \in \mathcal{I}},$$

with entries $u_{\mathbf{i}} = u^{(1)}_{i_1} \cdots u^{(d)}_{i_d}$. Storage: $dn << n^d$.

Definition 3. The canonical format, $\mathcal{C}_{R,\mathbf{n}}$

$$A_{(R)} = \sum_{k=1}^{R} c_k u^{(1)}_k \otimes \dots \otimes u^{(d)}_k, \quad c_k \in \mathbb{R}, \tag{1}$$

with normalised $u^{(\ell)}_k \in \mathbb{R}^n$ and the canonical rank $\leq R$.



Tucker tensor format

Definition. Given the rank parameter $\mathbf{r} = (r_1, \ldots, r_d)$, define the Tucker tensor format [Tucker '66].

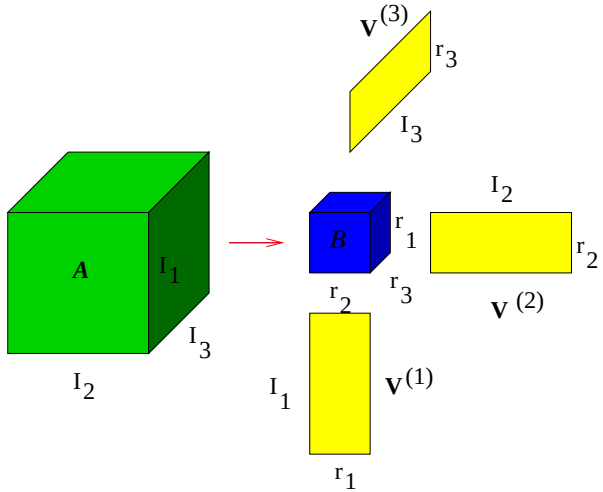
$$A_{(\mathbf{r})} = \sum_{\nu_1=1}^{r_1} \ldots \sum_{\nu_d=1}^{r_d} \beta_{\nu_1 \ldots \nu_d} \, v_{\nu_1}^{(1)} \otimes \ldots \otimes v_{\nu_d}^{(d)}, \tag{2}$$

with orthonormal $v_{\nu_\ell}^{(\ell)} \in \mathbb{V}_\ell = \mathbb{R}^{I_\ell}$ $(1 \le \nu_\ell \le r_\ell)$, and the core tensor

$$\boldsymbol{\beta} = [\beta_{\nu_1,\ldots,\nu_d}] \in \mathbb{B}_{\mathbf{r}} = \mathbb{R}^{r_1 \times \ldots \times r_d}$$

.

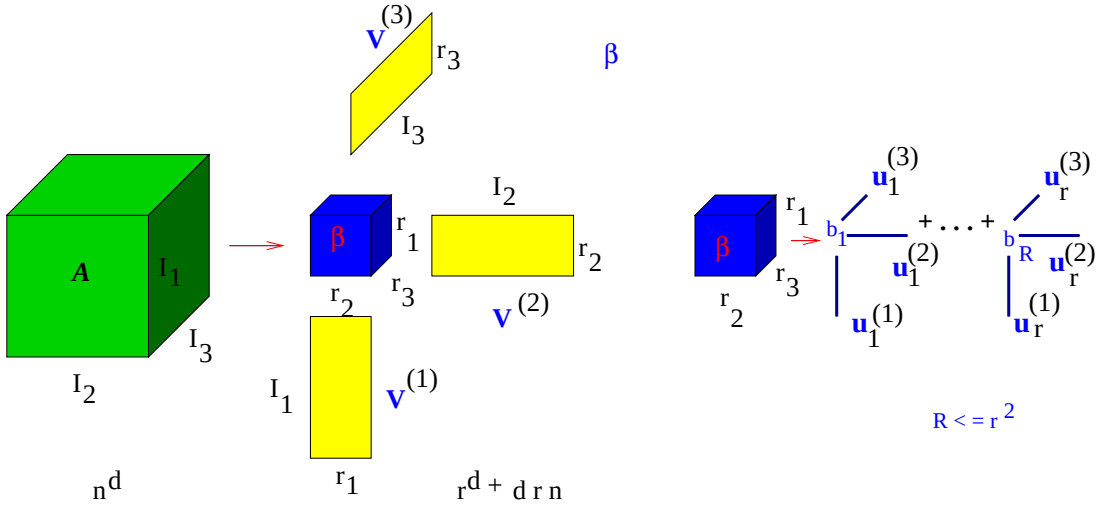
Using side matrices $V^{(\ell)} = [v_1^{(\ell)} \ldots v_{r_\ell}^{(\ell)}] \in \mathbb{R}^{n_\ell \times r_\ell}$ and tensor-by-matrix contracted product, $A_{(\mathbf{r})} = \boldsymbol{\beta} \times_1 V^{(1)} \times_2 V^{(2)} \times_3 \ldots \times_d V^{(d)}$.



Storage: $r^d + drn \ll n^d$.

Mixed Tucker-canonical (TC) tensor format

$$A_{(\mathbf{r})} = \left(\sum_{k=1}^{R} b_k \, u_k^{(1)} \otimes \ldots \otimes u_k^{(d)} \right) \times_1 V^{(1)} \times_2 V^{(2)} \times_3 \ldots \times_d V^{(d)}.$$



Advantages of the Tucker tensor decomposition:

1. Robust algorithm for approximating full format tensors of size n^d.
2. Rank reduction of the rank-R canonical tensors with large R.
3. Efficient for 3D tensors since r^3 is small.

Multilinear operations in canonical tensor format

$$A_1 = \sum_{k=1}^{R_1} c_k \, u_k^{(1)} \otimes \ldots \otimes u_k^{(d)}, \quad A_2 = \sum_{m=1}^{R_2} b_m \, v_m^{(1)} \otimes \ldots \otimes v_m^{(d)}.$$

Euclidean scalar product (complexity $O(dR_1R_2n) \ll n^d$),

$$\langle A_1, A_2 \rangle := \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} c_k \, b_m \prod_{\ell=1}^{d} \left\langle u_k^{(\ell)}, v_m^{(\ell)} \right\rangle.$$

Hadamard product of A_1, A_2

$$A_1 \odot A_2 := \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} c_k \, b_m \left(u_k^{(1)} \odot v_m^{(1)} \right) \otimes \ldots \otimes \left(u_k^{(d)} \odot v_m^{(d)} \right).$$

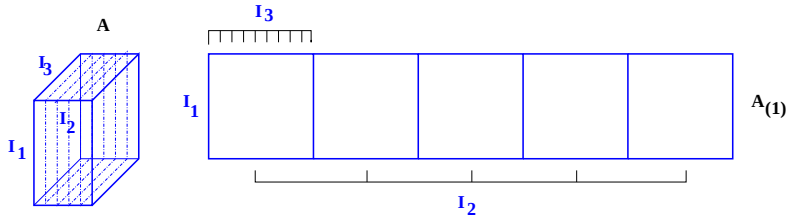
Convolution, for $d = 3$ (complexity $O(R_1R_2n \log n) \ll n^3 \log n$ (3D FFT))

$$A_1 * A_2 = \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} c_k \, b_m (u_m^{(1)} * v_k^{(1)}) \otimes (u_m^{(2)} * v_k^{(2)}) \otimes (u_m^{(3)} * v_k^{(3)})$$

The *unfolding of a tensor* along mode ℓ is a matrix

$$A_{(\ell)} = [a_{ij}] \in \mathbb{R}^{n_\ell \times (n_{\ell+1} \cdots n_d n_1 \cdots n_{\ell-1})}$$

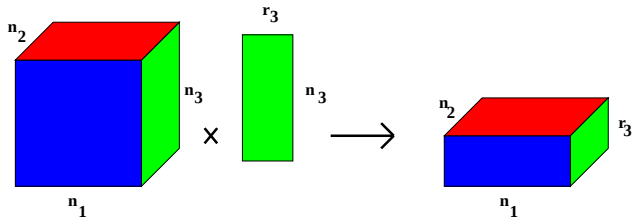
whose columns are the respective fibers along ℓ-mode.



Given a tensor $A \in \mathbb{R}^{I_1 \times \ldots I_d}$ and a matrix $M \in \mathbb{R}^{J_\ell \times I_\ell}$, we define the mode-$\ell$ tensor-matrix product by

$$B = A \times_\ell M \in \mathbb{R}^{I_1 \times \ldots \times I_{\ell-1} \times J_\ell \times I_{\ell+1} \ldots \times I_d},$$

where $b_{i_1,\ldots,i_{\ell-1},j_\ell,i_{\ell-1},\ldots,i_d} = \sum_{i_\ell=1}^{n_\ell} a_{i_1,\ldots,i_{\ell-1},i_\ell,i_{\ell-1},\ldots,i_d} m_{i_\ell,j_\ell}, \quad j_\ell \in J_\ell.$



Tucker tensor approximation

Multilinear algebra for the problems of chemometrics, psychometrics, data processing, etc.
[Tucker '66, De Lathauwer et al, 2000]

$$A_0 \in \mathbb{V}_{\mathbf{n}}: \quad f(A) := \|A_{(r)} - A_0\|^2 \to min \quad \text{over} \quad A \in \mathcal{T}_{\mathbf{r}}. \tag{3}$$

The minimisation problem is equivalent to the maximisation problem

$$g(V^{(1)}, ..., V^{(d)}) := \left\| A_0 \times_1 V^{(1)\,T} \times ... \times_d V^{(d)\,T} \right\|^2 \to max \tag{4}$$

over the set of $V^{(\ell)} \in \mathbb{R}^{n_\ell \times r_\ell}$.
For given $V^{(\ell)}$, the core $\boldsymbol{\beta}$ in minimizer of (3), $A_{(r)} = \boldsymbol{\beta} \times_1 V^{(1)} \times_2 \ldots \times_d V^{(d)}$ is

$$\boldsymbol{\beta} = A_0 \times_1 V^{(1)\,T} \times ... \times_d V^{(d)\,T} \in \mathbb{R}^{r_1 \times ... \times r_d}.$$

Complexity for $d = 3$, $O(n^4 + n^3 r + n^2 r^2 + n r^3)$, $r = \max_\ell r_\ell$.

For function related tensors, [B. Khoromskij 2006]:

$$\|A_{(r)} - A_0\| \le C e^{-\alpha r}, \text{ with } r = \min_\ell r_\ell.$$

Full-size tensor to Tucker

Algorithm ALS Tucker ($\mathbb{V}_{\mathbf{n}} \to \mathcal{T}_{\mathbf{r},\mathbf{n}}$). Given the input tensor $A \in \mathbb{V}_{\mathbf{n}}$.

1. Compute an initial guess $V_0^{(\ell)}$ ($\ell = 1, ..., d$) for the ℓ-mode side-matrices by truncated SVD applied to matrix unfolding $A_{(\ell)}$ (cost $O(n^{d+1})$).

2. For $k = 1 : k_{max}$ do: for each $q = 1, ..., d$, and with fixed side-matrices $V^{(\ell)} \in \mathbb{R}^{n \times r_\ell}$, $\ell \neq q$, optimise the side matrix $V^{(q)}$ via computing the dominating r_q-dimensional subspace (truncated SVD) for the respective matrix unfolding $B_{(q)} \in \mathbb{R}^{n \times \bar{r}_q}$, $\bar{r}_q = r_1 ... r_{q-1} r_{q+1} ... r_d$, corresponding to the q-mode contracted product

$$B_{(q)} = A \times_1 V^{(1)\,T} \times ... \times_{q-1} V^{(q-1)\,T} \times_{q+1} V^{(q+1)\,T} ... \times_d V^{(d)\,T}.$$

   Each iteration costs $O(dr^{d-1} n \min\{r^{d-1}, n\})$, since $\bar{r}_q = O(r^{d-1})$.

3. Compute the core $\boldsymbol{\beta}$ as the representation coefficients of the orthogonal projection of A onto $\mathbb{T}_{\mathbf{n}} = \otimes_{\ell=1}^d \mathbb{T}_\ell$ with $\mathbb{T}_\ell = \mathrm{span}\{v_\ell^\nu\}_{\nu=1}^{r_\ell}$,

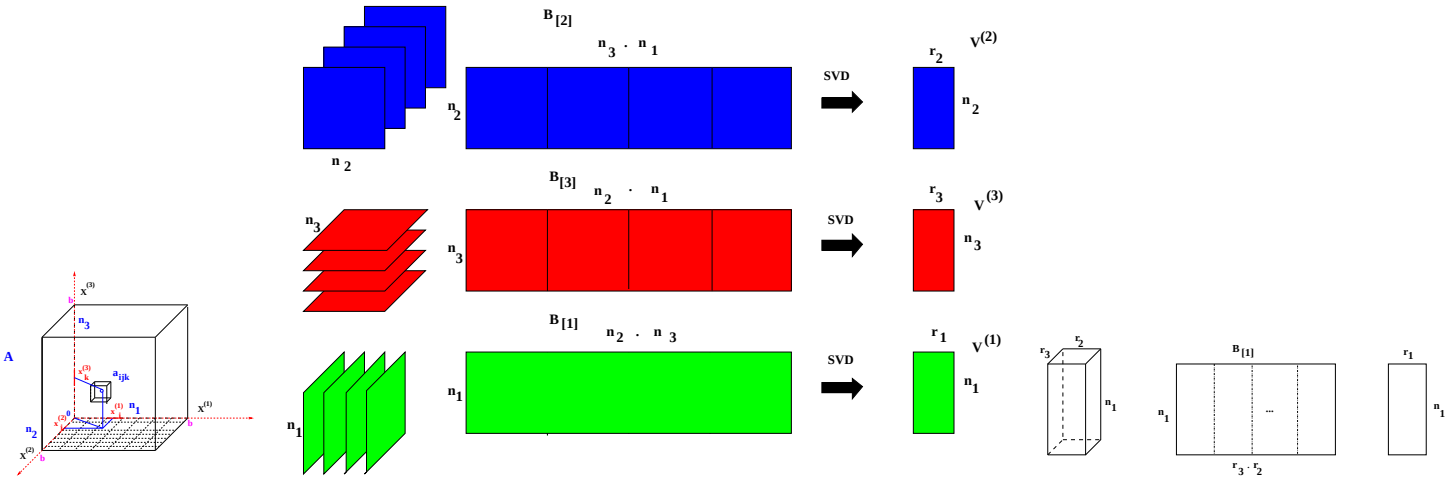
$$\boldsymbol{\beta} = A \times_1 V^{(1)\,T} \times ... \times_d V^{(d)\,T} \in \mathbb{B}_{\mathbf{r}},$$

   at the cost $O(r^d n)$.

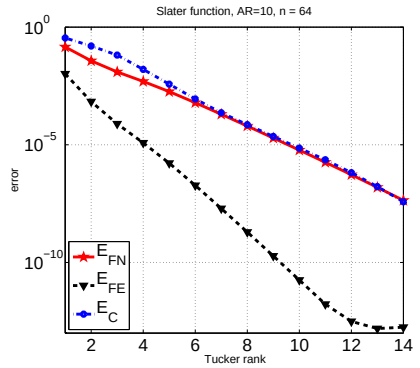
Functional Tucker approximation [B.N. Khoromskij, VKH '06 (CEJM '07)]

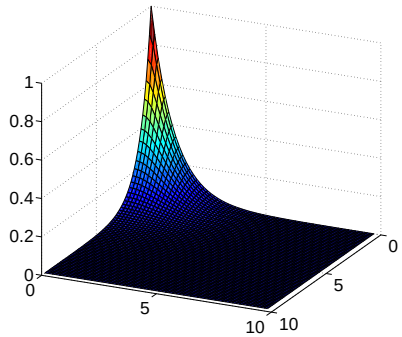
$f(x)$, $x = (x^{(1)}, x^{(2)}, x^{(3)})^T \in \mathbb{R}^3$ is discretized in $[a, b]^3$. Sampling points: $x_{i_\ell}^{(\ell)} = a_\ell + (i_\ell - \frac{1}{2})(\frac{b-a}{n_\ell})$, $i_\ell = 1, 2, \ldots n_\ell$.

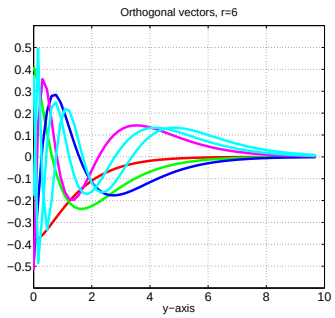
$\Rightarrow$ We generate a tensor $A \in \mathbb{R}^{n_1 \times n_2 \times n_3}$ with entries $a_{ijk} = f(x_i^{(1)}, x_j^{(2)}, x_k^{(3)})$.



Example: Slater function $f(x) = \exp(-\alpha\|x\|)$, $E_{FN} = \frac{\|A_0 - A_{(r)}\|}{\|A_0\|}$ $E_{FE} = \frac{\|A_0\| - \|A_{(r)}\|}{\|A_0\|}$, $E_C := \frac{\max_{i\in\mathcal{I}} |a_{0,i} - a_{r,i}|}{\max_{i\in\mathcal{I}} |a_{0,i}|}$.



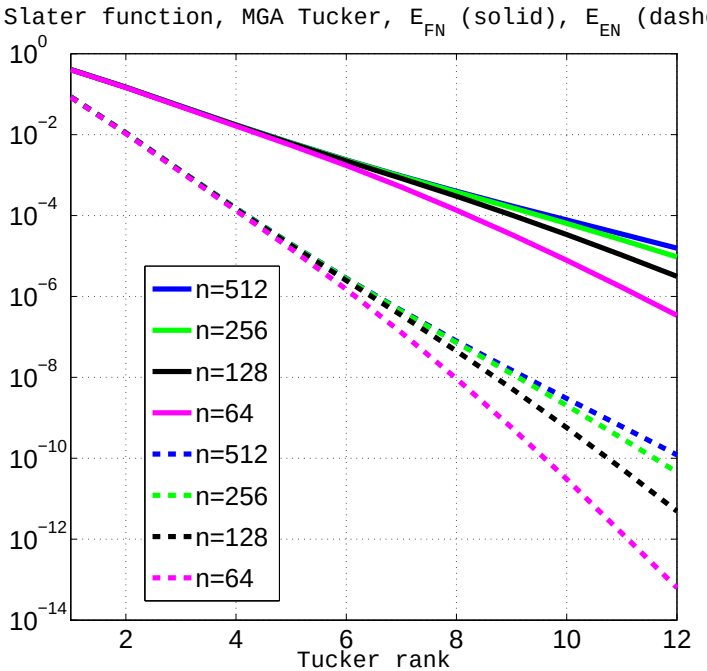


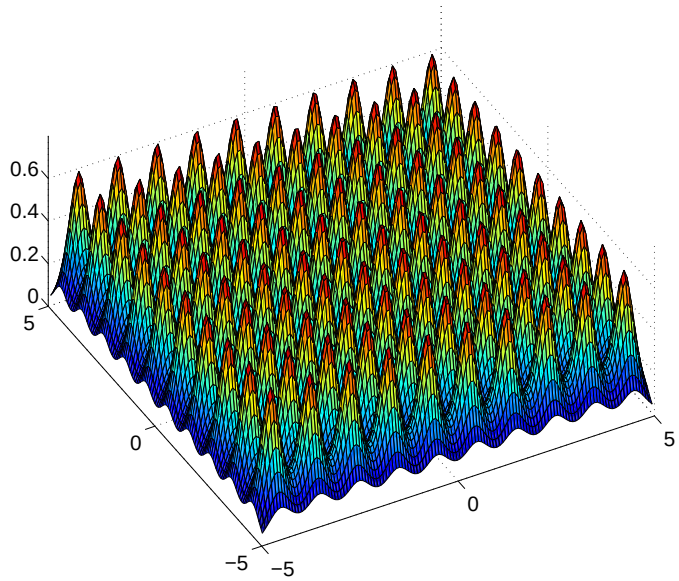


Multigrid Tucker for 3D periodic structures

[VKH '10 (TU Berlin, dissertation)]

Complexity for $d = 3$: $O(n^3)$ (instead of $O(n^4)$).





The "multi-centered Slater potential" obtained by displacing a single Slater potential with respect to the $m \times m \times m$ spatial grid of size $H > 0$, (here $m = 10$)

$$g(x) = \sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{k=1}^{m} e^{-\alpha \sqrt{(x_1 - iH)^2 + (x_2 - jH)^2 + (x_3 - kH)^2}}.$$

Canonical to Tucker Approximation

[B.N. Khoromskij, VKH '08 (SISC '09)] Theorem.
Let $A \in \mathcal{C}_{R,\mathbf{n}}$. Then the minimisation problem

$$A \in \mathcal{C}_{R,\mathbf{n}} \subset \mathbb{V}_{\mathbf{n}} : \quad A_{(\mathbf{r})} = \operatorname{argmin}_{V \in \mathcal{T}_{\mathbf{r},\mathbf{n}}} \|A - V\|_{\mathbb{V}_{\mathbf{r}}}, \tag{5}$$

$$[Z^{(1)}, ..., Z^{(d)}] = \operatorname{argmax}_{V^{(\ell)} \in \mathcal{M}_\ell} \left\| \sum_{\nu=1}^{R} c_\nu \left({V^{(1)}}^T u_\nu^{(1)} \right) \otimes ... \otimes \left({V^{(d)}}^T u_\nu^{(d)} \right) \right\|_{\mathbb{V}_{\mathbf{r}}}^2,$$

Init. guess: RHOSVD $Z_0^{(\ell)} \Rightarrow$ the truncated SVD of $U^{(\ell)} = [u_1^{(\ell)} ... u_R^{(\ell)}]$,
under the compatibility condition

$$r_\ell \le rank(U^{(\ell)}) \quad \text{with} \quad U^{(\ell)} = [u_1^{(\ell)} ... u_R^{(\ell)}] \in \mathbb{R}^{n \times R},$$

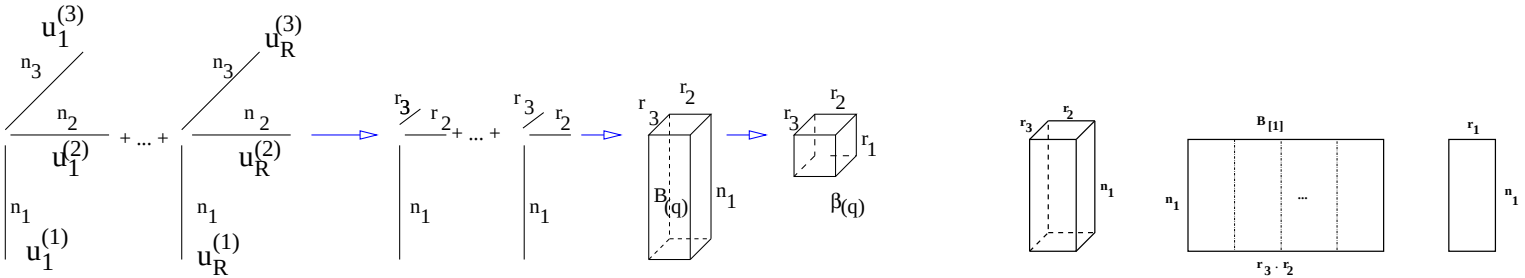
Error bounds for RHOSVD

$$\|A - A^0_{(\mathbf{r})}\| \le \|\mathbf{c}\| \sum_{\ell=1}^{d} \Big(\sum_{k=r_\ell+1}^{\min(n,R)} \sigma_{\ell,k}^2 \Big)^{1/2}, \qquad \text{where } \|\mathbf{c}\|^2 = \sum_{\nu=1}^{R} c_\nu^2.$$

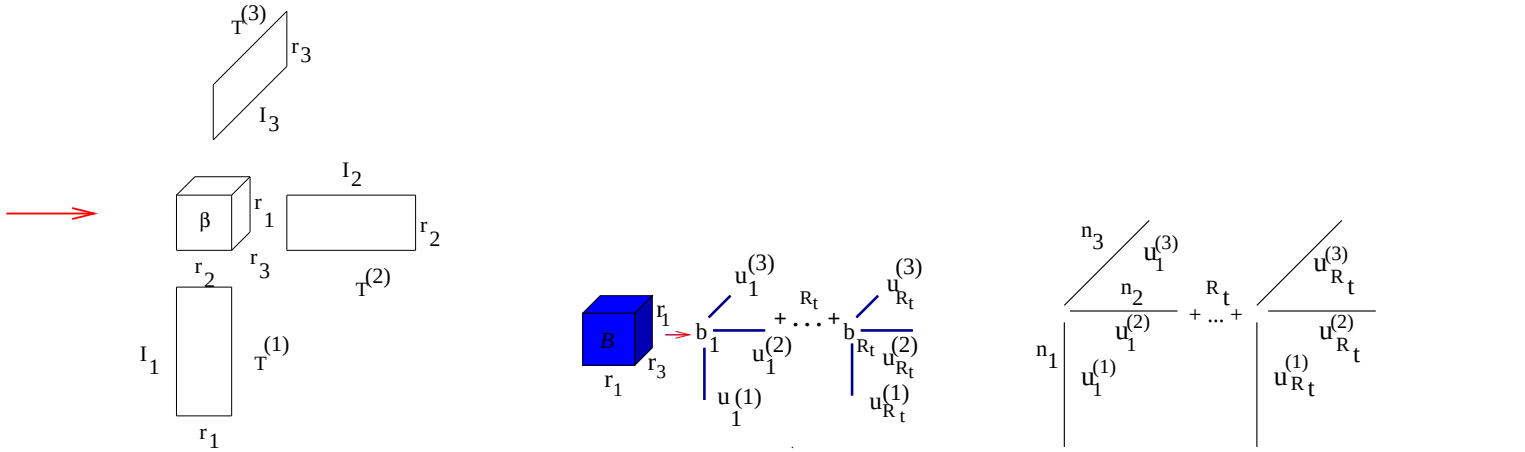
C2T + T2C rank reduction

[B.N. Khoromskij, VKH '07 (SICS '09)]

$$A = \sum_{k=1}^{R} c_k \otimes u_k^{(1)} \otimes_2 u_k^{(2)} \otimes_3 u_k^{(3)}$$



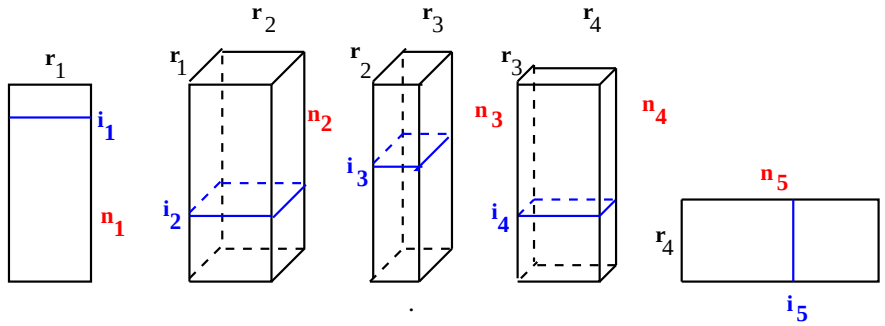
$$R_t \ll R, \quad R_t \le r^2$$



Tensor formats for higher dimensions

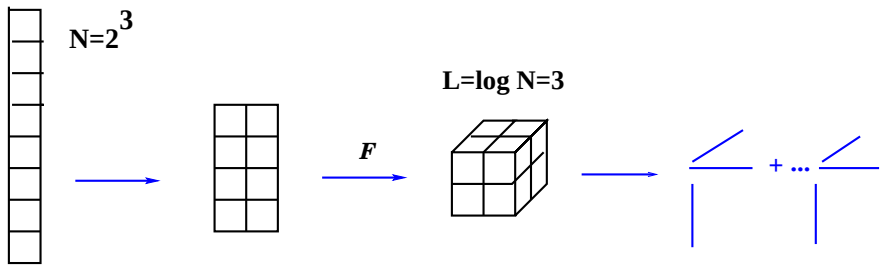
Matrix product states tensor factorization (MPS): [White 1992], [Cirac, Verstraete 2004] [Vidal 2003]
(reinvented as tensor train format by [Oseledets, Tyrtyshnikov 2009])

$$a_{i_1,i_2,i_3,i_4,i_5} = \prod_{k=1}^{5} B_k(i_k), \quad A \in \mathbb{R}^{n1 \times n_2 \times n3 \times n_4 \times n_5}, \quad B_k \in \mathbb{R}^{r_{k-1} \times r_k}, \quad r_0 = r_5 = 1.$$



Quantized tensor format (for function related vectors/tensors):[Khoromskij 2009, (CA '11)]

$$2^L >> 2Lr^2, \qquad r = 1 \text{ for } e^{-\alpha\|x\|}, \quad r = 2 \text{ for } sin(x), \text{ etc.}$$



Grid-based approaches and related tensor formats

- Sparse grids: M. Griebel, H. Yserentant, C.Schwab, et al. 1990.
- Wavelets with canonical format: G. Beylkin, M. Mohlenkamp (2002), R. Schneider, H.-J. Flad, W. Hackbusch, B. Khoromskij (2005).
- Functional Tucker, canonical-to-Tucker transform (2006-2008) tensor-structured numerical methods, 3D convolution integrals (2008) V. Khoromskaia, B. Khoromskij.
- 3D grid based solvers for the Hartree-Fock equation (2009-2012), 3D grid-based TEI (2011-12): V. Khoromskaia, B. Khoromskij, H.-J. Flad, R. Schneider.
- Matrix Product States, Tensor Train (TT): S. White (1992), Cirac, Verstraete (2004), I. Oseledets, E. Tyrtyshnikov (2009).
- Quantized vector/tensor low rank approximation: B. Khoromskij (2009).
- QTT library: I. Oseledets, B. Khoromskij, S. Dolgov, et. al. (2009-2012).
- Hierarchical Tucker, hierarchical SVD of tensors: W. Hackbusch, L. Grasedyck (2009). D. Kressner, C. Tobler, (2010)
- Best TT approximation: R. Schneider, T. Rohwedder, S. Holtz (2010-2012).

The Hartree-Fock equation, standard Galerkin scheme

Nonlinear eigenvalue problem

$$\mathcal{F}\varphi_i(x) \equiv (-\frac{1}{2}\Delta + V_c + V_H - \mathcal{K})\varphi_i(x) = \lambda_i\,\varphi_i(x), \qquad i = 1, ..., N_{orb}.$$

The Fock operator $\mathcal{F}$ depends on $\tau(x,y) = 2\sum\limits_{i=1}^{N_{orb}} \varphi_i(x)\varphi_i(y)$,

$$\mathcal{F}\varphi := [-\frac{1}{2}\Delta - \sum_{\nu=1}^{M} \frac{Z_\nu}{\|x - a_\nu\|} + \int_{\mathbb{R}^3} \frac{\tau(y,y)}{\|x-y\|}\,dy]\varphi - \frac{1}{2}\int_{\mathbb{R}^3} \frac{\tau(x,y)}{\|x-y\|}\,\varphi(y)dy.$$

Numerical challenges: high accuracy, 3D and 6D singular integrals, strong nonlinearity.

Standart computational scheme.

Expansion of molecular orbitals in $\{g_\mu\}_{1\le\mu\le N_b}$,

$$\varphi_i(x) = \sum_{\mu=1}^{N_b} c_{i\mu} g_\mu(x), \quad i = 1, ..., N_{orb},$$

yields the Galerkin system of nonlinear equations for coefficients matrix $C = \{c_{i\mu}\} \in \mathbb{R}^{N_{orb}\times N_b}$, (and density matrix $D = 2CC^* \in \mathbb{R}^{N_b\times N_b}$)

$$F(C)C = SC\Lambda, \quad \Lambda = diag(\lambda_1, ..., \lambda_{N_b}), \quad C^T SC = I_{N_b},$$

where $F(C) = H + J(C) + K(C)$.

Standard Galerkin scheme

Precomputed: core Hamiltonian $H = \{h_{\mu\nu}\}$

$$h_{\mu\nu} = \frac{1}{2}\int_{\mathbb{R}^3} \nabla g_\mu \cdot \nabla g_\nu dx + \int_{\mathbb{R}^3} V_c(x) g_\mu g_\nu dx \quad 1 \le \mu, \nu \le N_b.$$

and two-electron integrals (TEI)

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

Then the EVP

$$F(C)C = SC\Lambda$$

is solved iteratively, using DIIS [Pulay '80] and updating $F(C) = H + J(C) + K(C)$,

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

The ground state energy

$$E_{HF} = 2\sum_{i=1}^{N_{orb}} \lambda_i - \sum_{i=1}^{N_{orb}} \left(\widetilde{J}_i - \widetilde{K}_i\right),$$

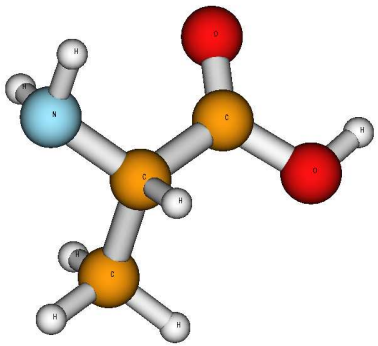
where $\widetilde{J}_i = (\varphi_i, V_H\varphi_i)$ and $\widetilde{K}_i = (\varphi_i, K\varphi_i)$.

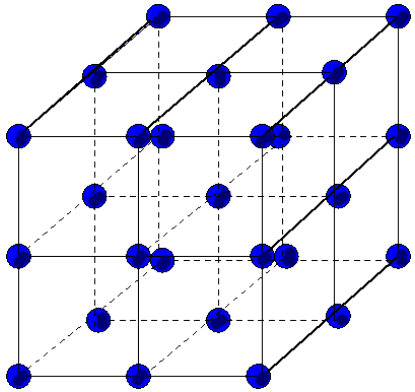
Competing grid-based tensor approach to computational quantum chemistry

Benchmark packages (analytic): MOLPRO [Werner et al.], GAUSSIAN, CRYSTAL, ...

Grid-based tensor methods in HF calculations: [Khoromskij, VKH, Flad, 2009, SISC '11],

- Example of a **compact molecule** computed by tensor method: Alanin aminoacid
- 3D lattice structure





- Grid-based tensor numerical methods look promising for computation of structured **extended systems** and periodic compounds.

Basic building blocks

[VKH, Khoromskij '08 - '13]

- **Canonical, Tucker and QTT** tensor arithmetics.
- Grid basis $\{g_\mu\}$, and core Hamiltonian in ($O(n)$ and $O(\log n)$ operations.
- **Fast 3D tensor convolution** in $O(n \log n)$ operations.
- Direct/redundancy free **factorizations of TEI** matrix $B = [b_{\mu\nu;\kappa\lambda}] \in \mathbb{R}^{N_b^2 \times N_b^2}$.
- **Cholesky decomposition** (ε-approximation) of B:

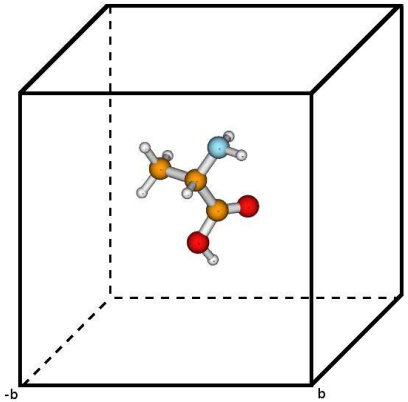
Compute columns and diagonal of B using precomputed factorization,

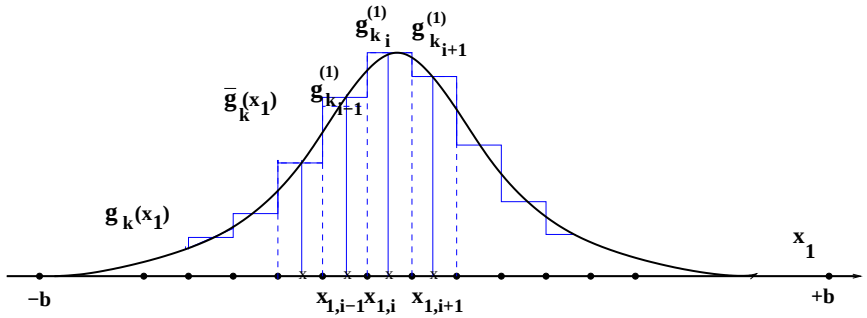
$$B = mat(\mathbf{B}) := [b_{\mu\nu,\kappa\lambda}] \approx LL^T, \quad R_B = rank_\varepsilon(B) = O(N_b).$$

QTT compression of the Cholesky factor $L \in \mathbb{R}^{N_b^2 \times R_B}$: $N_b^2 \Rightarrow N_{orb}^2$, $N_b \approx 10 N_{orb}$.

- **DIIS** self-consistent iteration (standard in quantum chemistry).
- **MP2** energy correction via tensor factorizations.

Discretization of 3D basis functions





The computational box: $[-b, b]^3, \quad b \approx 15 \overset{\circ}{A}$
$n \times n \times n$ 3D Cartesian grid, $n \sim 10^5$

$$g_k(x) = p_k(x_1, x_2, x_3) e^{\alpha_k (x_1^2 + x_2^2 + x_3^2)}$$

the continuous basis functions $g_k(x)$: $\mathbf{I}_0 : g_k \to \overline{g}_k := \sum_{\mathbf{i} \in \mathcal{I}} g_k(x_\mathbf{i}) \zeta_\mathbf{i}(x)$.

$$g_k(x) \approx \mathbf{I}_0 g_k := \overline{g}_k(x) = \prod_{\ell=1}^3 \overline{g}_k^{(\ell)}(x_\ell) = \prod_{\ell=1}^3 \sum_{i_\ell=1}^n g_k^{(\ell)}(x_{\ell,i_\ell}) \zeta_{i_\ell}^{(\ell)}(x_\ell), \ \ell = 1, 2, 3$$

rank-1 tensors: $\mathbf{G}_k = G_k^{(1)} \otimes G_k^{(2)} \otimes G_k^{(3)}$, with $G_k^{(\ell)} = \{g_k^{(\ell)}(x_{\ell,i_\ell})\}_{i_\ell=1}^n \in \mathbb{R}^{I_\ell}$.

Example: 3D grid-based Hartree potential in 1D complexity

$$V_H(x) := \int_{\mathbb{R}^3} \frac{\rho(y)}{\|x-y\|}\, dy \qquad \rho(x) = 2\sum_{a=1}^{N_{orb}} (\varphi_a)^2, \quad x \in \mathbb{R}^3$$

$$\varphi_a(x) = \sum_{\mu=1}^{N_b} c_{a\mu} g_\mu(x), \quad a = 1, ..., N_{orb},$$

$$\begin{aligned} \rho \approx \mathbf{\Theta} : &= \sum_{a=1}^{N_{orb}} \left(\sum_{\kappa=1}^{N_b} \sum_{\lambda=1}^{N_b} c_{\kappa a} c_{\lambda a} \mathbf{G}_\kappa \odot \mathbf{G}_\lambda \right) \\ &= \sum_{m=1}^{R_\rho} c_m u_m^{(1)} \otimes u_m^{(2)} \otimes u_m^{(3)}, \quad u_m^{(\ell)} = G_\kappa^{(\ell)} \odot G_\lambda^{(\ell)} \in \mathbb{R}^n. \end{aligned}$$

$R_\rho(CH_4) = 1540, \quad R_\rho(C_2H_6) = 4656, \quad R_\rho(H_2O) = 861$

Multigrid C2T + T2C tensor rank reduction: $\mathbf{\Theta} \Rightarrow \mathbf{\Theta}'$

$rank(\mathbf{\Theta}) \approx 10^4 \quad \Rightarrow \quad rank(\mathbf{\Theta}') \sim 10^2.$

Example: 3D grid-based Hartree potential in 1D complexity [Khoromskij, VKH '08 (SISC 2009)]

The Newton kernel $P_N = \left[\langle \frac{1}{\|x\|}, \zeta_{\mathbf{i}} \rangle\right]$, $\zeta_{\mathbf{i}}$ p.w.c.,
by *sinc*-quadratures. $\mathrm{Rank}(P_N) \sim 20 \div 30$. [Bertoglio, Khoromskij '08 (CPC 2012)]

The tensor-product convolution [Khoromskij '08], (accuracy $O(h^2)$)

$$\begin{aligned} V_H &= \rho * \frac{1}{\|\cdot\|} \approx \Theta' * P_N \\ &= \sum_{m'=1}^{R_{\rho_r}} \sum_{k=1}^{R_N} c_{m'} b_k \left(u_{m'}^{(1)} * v_k^{(1)}\right) \otimes \left(u_{m'}^{(2)} * v_k^{(2)}\right) \otimes \left(u_{m'}^{(3)} * v_k^{(3)}\right). \end{aligned}$$

The Coulomb matrix

$$J(C)_{\mu\nu} = \int_{R^3} g_\mu(x) V_H(x) g_\nu(x) dx \approx \int_{\mathbb{R}^3} \overline{g}_\mu(x) V_H(x) \overline{g}_\nu(x)$$
$$\approx \langle G_\mu \odot G_\nu, \Theta' * P_N \rangle, \quad 1 \le \mu, \nu \le N_b.$$

$W_{C*C} = O(R_{\rho_r} R_N n \log n)$

Tensor-product convolution vs. 3D FFT

[Khoromskij, VKH '08 (SISC 2009)]

The cost of computation of V_H by tensor product convolution (1D FFT):

$$\mathcal{N}_{C*C} = O(R_{\rho_r} R_N n \log n)$$

instead of $O(n^3 \log n)$ for 3D FFT.

n^3	128^3	256^3	512^3	1024^3	2048^3	4096^3	8192^3	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	157.5	299.2
C2T	4.2	4.7	5.6	6.9	10.9	20.0	37.9	86.0

CPU time (in sec) for the computation of V_H for H_2O.

(3D FFT time for $n \geq 1024$ is obtained by extrapolation).

Example 2: TS computation of the exchange matrix

[VKH, 2010]

$$K_{k,m} := \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} g_k(x)\frac{\varphi_a(x)\varphi_a(y)}{|x-y|}g_m(y)dxdy, \quad k,m = 1,\dots N_b$$

1. Convolution

$$W_{a,m}(x) = \int_{\mathbb{R}^3}\frac{\varphi_a(y)g_m(y)}{|x-y|}dy \approx \overline{W}_{a,m} := \left[G_m \odot \sum_{\nu=1}^{N_b} c_{\nu a} G_\nu\right] * P_N,$$

2. Scalar products

$$V_{km,a} = \int_{\mathbb{R}^3}\varphi_a(x)g_k(x)W_{a,m}(x)dx \approx \overline{V}_{km,a} := \langle G_k \odot \left[\sum_{\mu=1}^{N_b} c_{\mu a} G_\mu\right], \overline{W}_{am}\rangle.$$

3. The exchange matrix

$$K_{k,m} = \sum_{a=1}^{N_{orb}} \overline{V}_{km,a}.$$

Grid-based two-electron integrals (TEI)

[VKH, Khoromskij, Schneider, '12]

$$b_{\mu\nu\kappa\lambda} = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{g_\mu(x)g_\nu(x)g_\kappa(y)g_\lambda(y)}{\|x-y\|}\,dxdy = \langle \mathbf{G}_\mu \odot \mathbf{G}_\nu, \mathbf{P}_{\mathcal{N}} * (\mathbf{G}_\kappa \odot \mathbf{G}_\lambda)\rangle_{n^{\otimes 3}},$$

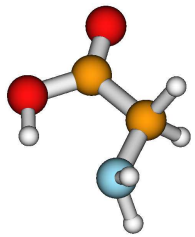
$$\mathbf{G}_\mu = G_\mu^{(1)} \otimes G_\mu^{(2)} \otimes G_\mu^{(3)} \in \mathbb{R}^{n\times n\times n}.$$

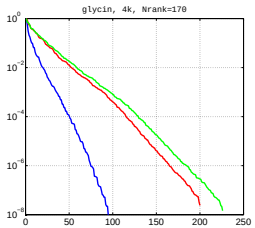
$$G^{(\ell)} = \left[G_\mu^{(\ell)} \odot G_\nu^{(\ell)}\right]_{1\le\mu,\nu\le N_b} \in \mathbb{R}^{n\times N_b^2} \quad \ell = 1,2,3.$$

Factorization ("1D density fitting") by Cholesky decomposition of $G^{(\ell)}G^{(\ell)\,T}$:

$$G^{(\ell)} \cong U^{(\ell)}V^{(\ell)\,T}, \quad U^{(\ell)} \in \mathbb{R}^{n\times R_\ell}, \quad V^{(\ell)} \in \mathbb{R}^{N_b^2\times R_\ell},$$

$\Rightarrow$ number of convolutions is reduced from N_b^2 to $R_\ell \le N_b$,
$n = 32768$ (up to 131072),
$N_b^2 \sim 28000$ (40000 for alanine):





ε-rank reduction for glycine:
from $N_b^2 = 28900$, to $R_\ell \sim 100 \div 220$.

Fast convolution via tensor approximation of Green's kernel

Tensor approximation of the Newton kernel using Laplace transform and sinc-quadratures:

[Gavrilyuk, Hackbusch, Khoromskij '08]

[Bertoglio, Khoromskij '10]

Green's function for Δ in $\mathbb{R}^3$, via $(2M+1)$-term sinc-quadrature approximation

$$\frac{1}{\|x\|} = \int_0^\infty e^{-t^2\|x\|^2} dt \approx \sum_{k=-M}^{M} c_k e^{-t_k^2\|x\|^2} = \sum_{k=-M}^{M} c_k \prod_{\ell=1}^{3} e^{-t_k^2 x_\ell^2} \quad \mapsto \mathbf{P}_{\mathcal{N}}.$$

$\mathbf{P}_{\mathcal{N}} \in \mathbb{R}^{n\times n\times n}$, can. rank of $\mathbf{P}_{\mathcal{N}}$ $R_{\mathcal{N}} \le 30$.

Tensor-product convolution, $O(n \log n)$:

[Khoromskij '08]

[Khoromskij, Khoromskaia '09]

$$U * P_N = \sum_{k=1}^{R_F} \sum_{m=1}^{R_N} c_k b_m (u_m^{(1)} * p_k^{(1)}) \otimes (u_m^{(2)} * p_k^{(2)}) \otimes (u_m^{(3)} * p_k^{(3)})$$

n^3	512^3	1024^3	2048^3	4096^3	8192^3	16384^3	32768^3
FFT_3	37.5	350.6	~ 3500	–	–	–	~ 1.2 years
$C_{R_F} * C_{R_{\mathcal{N}}}$	2.4	6.7	14.6	44	107	236	535

CPU time (in sec) for TEI: $\frac{1}{\|x\|} * g_\mu g_\nu$, $\mu, \nu = 1, ..., N_b$, $\varepsilon = 10^{-7}$,

H_2O, $N_b = 41$, $\frac{N_b(N_b+1)}{2} \mapsto R_F = 71$, $R_{\mathcal{N}} = 27$.

Factorized TEI

The Newton kernel: $P^{(\ell)} \in \mathbb{R}^{n \times R_{\mathcal{N}}}$ are the factor matrices in the rank-$R_{\mathcal{N}}$ canonical tensor $\mathbf{P}_{\mathcal{N}} \in \mathbb{R}^{n \times n \times n}$.

$$B \cong B_{\varepsilon} := \sum_{k=1}^{R_{\mathcal{N}}} \odot_{\ell=1}^{3} V^{(\ell)} M_k^{(\ell)} V^{(\ell)\,T} \in \mathbb{R}^{N_b^2 \times N_b^2}$$

with the convolution matrix

$$M_k^{(\ell)} = U^{(\ell)\,T} (P_k^{(\ell)} *_n U^{(\ell)}) \in \mathbb{R}^{R_\ell \times R_\ell}, \quad k = 1, ..., R_{\mathcal{N}}.$$

The diagonal elements and j-column in the TEI matrix B :

$$B(i,i) = \sum_{k=1}^{R_{\mathcal{N}}} \odot_{\ell=1}^{3} V^{(\ell)}(:,i) M_k^{(\ell)} V^{(\ell)}(:,i)^T.$$

$$B(:,j) = \sum_{k=1}^{R_{\mathcal{N}}} \odot_{\ell=1}^{3} V^{(\ell)} M_k^{(\ell)} V^{(\ell)}(:,j)^T,$$

Cholesky decomposition (ε-approximation)

$$B := mat(\mathbf{B}) = [b_{\mu\nu,\kappa\lambda}] \approx LL^T, \quad L \in \mathbb{R}^{N_b^2 \times R_B},$$

with $R_B \sim N_b$.

Representation complexity of $\mathbf{B}$ using the quantized tensor format can be reduced to $O(N_b N_{orb}^2)$ (instead of $O(N_b^3)$). ($N_b \sim 10 N_{orb}$).

Laplacian in Gaussian basis

[VKH, Andrae, Khoromskij, CPC'12]

For a function in Gaussian basis $\{g_k(x)\}_{1\le k\le N_b}$, $x\in\mathbb{R}^3$, the 3D Laplace operator

$$A_g = \{a_{km}\} \in \mathbb{R}^{N_b\times N_b} \quad \text{with } a_{km} = \langle \Delta g_k(x), g_m(x)\rangle.$$

The discete 3D Laplace operator $\Delta_3 \in \mathbb{R}^{n^3\times n^3}$

$$\Delta_3 = \Delta_1^{(1)}\otimes I^{(2)}\otimes I^{(3)} + I^{(1)}\otimes \Delta_1^{(2)}\otimes I^{(3)} + I^{(1)}\otimes I^{(2)}\otimes \Delta_1^{(3)},$$

where $\Delta_1 = \frac{1}{h} tridiag\{-1,2,-1\}$.
Given $\mathbf{G}_k = G_k^{(1)}\otimes G_k^{(2)}\otimes G_k^{(3)}$, $A_g \approx A_G = \{\overline{a}_{km}\}$,

$$\begin{aligned}
\overline{a}_{km} &= \langle \Delta_1 G_k^{(1)}, G_m^{(1)}\rangle\langle G_k^{(2)}, G_m^{(2)}\rangle\langle G_k^{(3)}, G_m^{(3)}\rangle \\
&\quad + \langle G_k^{(1)}, G_m^{(1)}\rangle\langle \Delta_1 G_k^{(2)}, G_m^{(2)}\rangle\langle G_k^{(3)}, G_m^{(3)}\rangle \\
&\quad + \langle G_k^{(1)}, G_m^{(1)}\rangle\langle G_k^{(2)}, G_m^{(2)}\rangle\langle \Delta_1 G_k^{(3)}, G_m^{(3)}\rangle \\
&= \langle \Delta_3 \mathbf{G}_k, \mathbf{G}_m\rangle.
\end{aligned}$$

Complexity ($O(n)$).

Quantized tensor approximation of $O(\log n)$ complexity introduced in [Khoromskij '09,'11] is used for quantized tensor calculation of the Laplacian in [Kazeev, Khoromskij, '12],

Laplacian in Gaussian basis

[VKH, '13]

p	15	16	17	18	19	20
$n^3 = 2^{3p}$	32767^3	65535^3	131071^3	262143^3	524287^3	1048575^3
$err(A_G)$	0.0027	$6.8 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$4.2 \cdot 10^{-5}$	$1.0 \cdot 10^{-5}$	$2.6 \cdot 10^{-6}$
RE	-	$1.0 \cdot 10^{-5}$	$8.3 \cdot 10^{-8}$	$2.6 \cdot 10^{-9}$	$3.3 \cdot 10^{-10}$	0
time (sec)	12.8	17.4	25.7	42.6	77	135
Δa_{11}	49	12	3	0.7	0.19	0.0480
RE	-	0.3	0.0014	$3.3 \cdot 10^{-5}$	$3.3 \cdot 10^{-5}$	$3.3 \cdot 10^{-5}$

3D grid-based quantized tensor calculations for the water molecule (H_2O): accuracy and times vs 3D grid size for the Laplace Galerkin matrix $err(A_G)$ (discretized basis of $N_b = 41$ Cartesian Gaussians).

Tensor-based nuclear potential

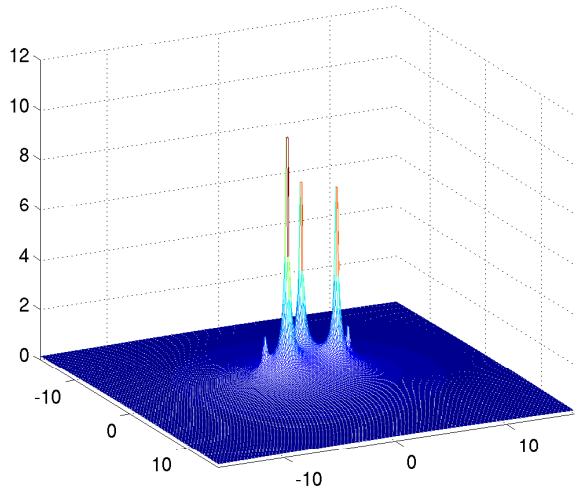
[VKH, Andrae, Khoromskij, CPC'12]

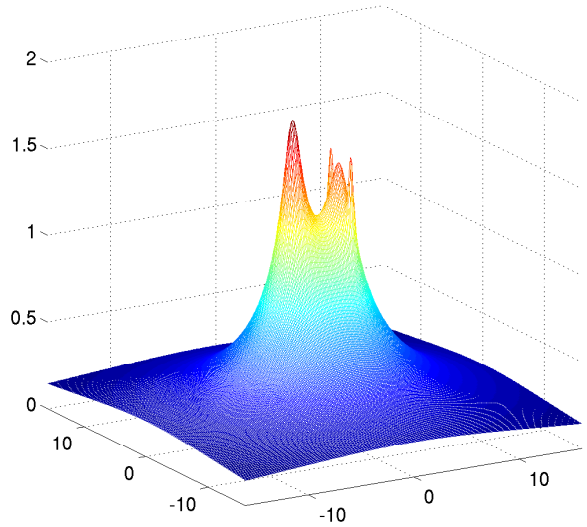
[VKH, '13]

$$V_c(x) = -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{\|x - a_\alpha\|}, \quad Z_\alpha > 0, \quad a_\alpha \in \mathbb{R}^3, \qquad \mathbf{P}_c = \sum_{\alpha=1}^{M} Z_\alpha \mathbf{P}_{c,\alpha},$$

$$\overline{v}_{km} = \int_{\mathbb{R}^3} V_c(x)\overline{g}_k(x)\overline{g}_m(x)dx \approx \langle \mathbf{G}_k \odot \mathbf{G}_m, \mathbf{P}_c \rangle, \quad 1 \le k, m \le N_b.$$

V_c for ethanol molecule (C_2H_5OH) at two levels: $z = 0$ and $z = 0.75$ au,





Tensor-based Core Hamiltonian

Laplace and nuclear potential calculations for CH_4, ($N_b = 55$).
Difference between the 3D grid-based and analytical calculations in Galerkin matrices

$$Er(A_G) = \frac{\|A_g - A_G\|}{\|A_g\|}, \quad Er(V_G) = \frac{\|V_g - V_G\|}{\|V_g\|}.$$

$N^3 = 2^{3p}$	8192^3	16384^3	32768^3	65536^3	131072^3
h(in au)	0.0036	0.0018	$8.9 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$
$Er(A_G)$	0.02	0.052	0.0013	$3.2 \cdot 10^{-4}$	$8 \cdot 10^{-5}$
RE	-	$2.6 \cdot 10^{-4}$	0	$2.0 \cdot 10^{-6}$	$1.7 \cdot 10^{-8}$
$Er(V_G)$	0.012	0.0029	$7.0 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$4.3 \cdot 10^{-5}$
RE	-	$2.6 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$3.0 \cdot 10^{-6}$	$1.2 \cdot 10^{-7}$

Note: $2.2 \cdot 10^{-4} au = 1.164$ Å $= 11.64$ femtometers (10^{-15} m), which is $\sim$ to size of atomic radii in a molecule.
(Atomic radius of Oxygen is 60 pm, Hydrogen 25 pm.)

$1fm = 10^{-15}$ m, $1pm = 10^{-12}$ m, 1 Å$= 10^{-10}$ m.

Self-consistent iteration for nonlinear EVP

[VKH, '13, preprint]

[VKH, Khoromskij '13]

EVP algorithm for black-box solver:

$$F(C)C = SC\Lambda, \quad F = H_0 + J(C) - K(C),$$

- Initial guess for $J = 0$, $K = 0$, $F(0) = H_0$.
- solve EVP $[H_0 + J(C) - K(C)]C = SC\Lambda$.
- Update of $J(C)$ and $K(C)$:
  ▷ Coulomb matrix: given $\overline{D} = vec(D)$,

$$vec(J) = B\overline{D} \approx L(L^T\overline{D}).$$

  ▷ HF exchange: using $D = 2CC^T$ and $B = LL^T$,

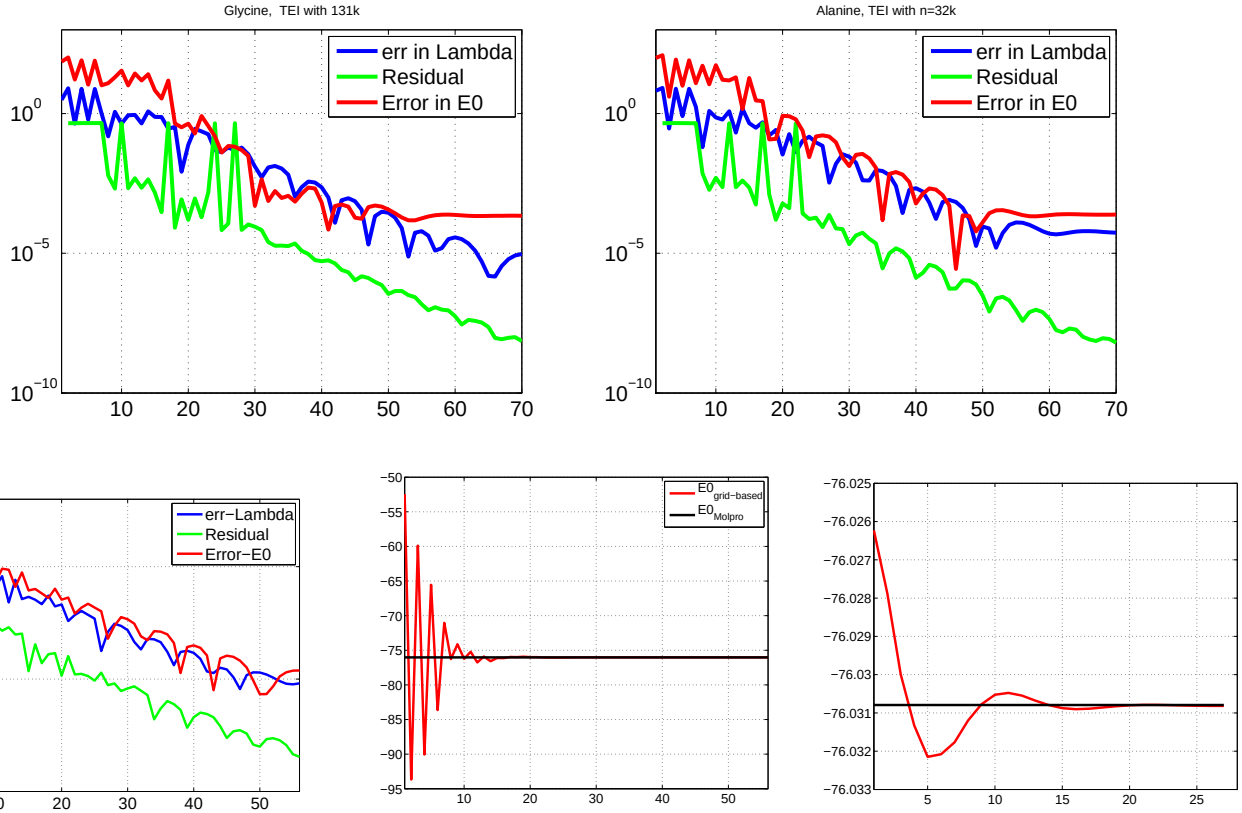
$$K(D)_{\mu\nu} = -\sum_{i=1}^{N_{orb}}\sum_{k=1}^{R_B}(\sum_{\lambda} L_{\mu\lambda k}C_{\lambda i})(\sum_{\kappa} C_{\kappa i}L_{\kappa\nu k}),$$

  $[L_{\mu\nu k}] = reshape(L, [N_b, N_b, R_B])$ is the $N_b \times N_b \times R_B$-folding of the Cholesky fact. L.
- DIIS for providing convergence.

TEI based nonlinear 3D EVP solver

[VKH, 2013]

DIIS iteration for amino acids glycine (C_2 H_5N O_2) with TEI on $n^3 = 131072^3$ and alanine (C_3H_7N O_2) with TEI on $n^3 = 32768^3$.



H_2O: iteration with core Hamiltonian on 131072^3; convergence in energy; last $k + 27$ iterations.

Grid-based calculations of large extended/periodic systems

[VKH, Khoromskij Preprint MIS MPG'13]

Main ingredients in tensor approach:

- Computing large lattice sums of the Newton kernels.
- Lattice-structured TEI computation.
- Block-structured representation of the Fock matrix.
- Fast diagonalisation of the Fock matrix.

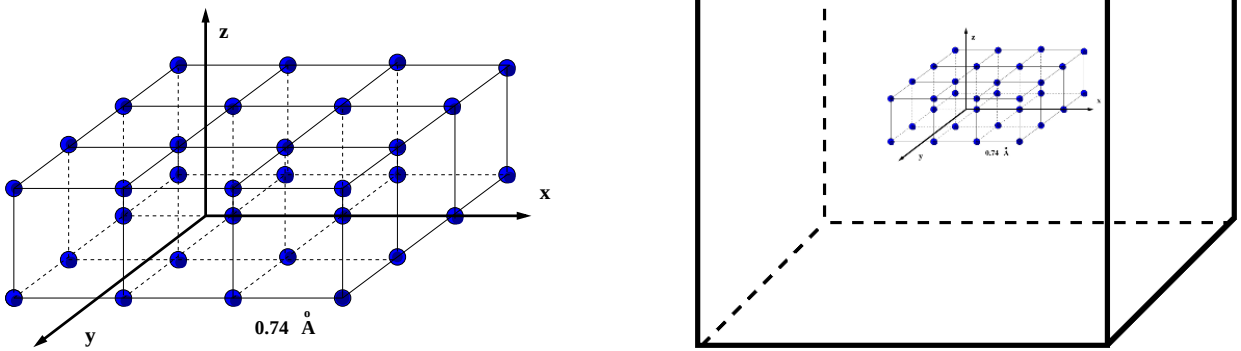
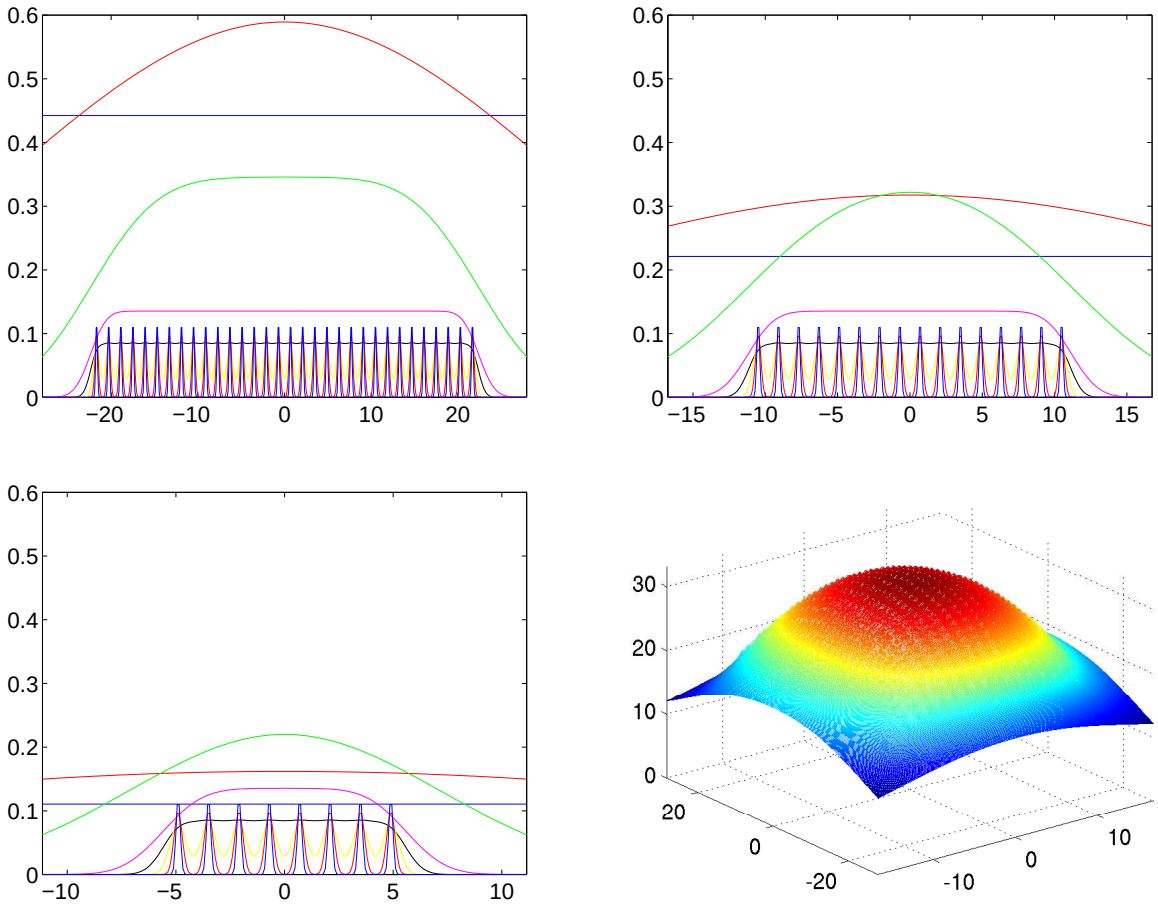


Figure: The periodic structure of the size $4.5 \times 4.5 \times 1.5$ $\overset{\circ}{A}^3$ in the box $[-b, b]^3$, with $b = 16$ au (~ 8.5 $\overset{\circ}{A}$).

Lattice sums of electrostatic potentials by assembled tensor approximation

Fast and accurate calculation of lattice sums of electrostatic potentials (absolute accuracy 10^{-14})



Assembled vectors along x- y- and z-axis, for a cluster of $32 \times 16 \times 8$ Hydrogen atoms in a rectangular box of size $\sim 55.4 \times 33.6 \times 22.4$ au^3 (Dirichle bound. cond.).
The resulting sum of 4096 nuclei potentials at cross-section with $z = 0.83$ au.

A sum of 10^6 potentials is computed in several seconds in Matlab. 3D grids $n^3 = 16384^3$

Resume

- Development of the tensor-structured numerical methods resulted in a "black box" solver for the Hartree-Fock equation in a general basis.
- Grid-based calculation of 3D integral operators with linear scaling in 1D.
- Grid-based 3D Laplace and nuclear potential operators with controllable accuracy.
- Two-electron integrals in a general basis.
- General bases can include any physically relevant functions (local finite elements, AO, Slater, truncated plane waves, etc).
- Robust tensor rank reduction algorithms (C2T+T2C, ACA+QR, etc.).
- Numerical tests for compact molecules confirm efficiency of algorithms.
- TS numerical methods applicable to post-HF models: MP2.
- Tensor numerical methods have a big potential for periodic and quasi-periodic structures.

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Thank you for attention

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