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QTT Representation of the Hartree and Exchange Operators in Electronic Structure Calculations

(revised version: September 2011)

by

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Preprint no.: 37 2011

QTT Representation of the Hartree and Exchange Operators in Electronic Structure Calculations*

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Abstract

In this paper, the tensor-structured numerical evaluation of the Coulomb and exchange operators in the Hartree-Fock equation is supplemented by the usage of recent quantized-TT (QTT) formats. It leads to $O(\log n)$ complexity at computationally extensive stages in the rank-structured calculation with the respective 3D Hartree and exchange potentials discretized on large $n \times n \times n$ Cartesian grids. The numerical examples for some volumetric organic molecules confirm that the QTT ranks of these potentials are nearly independent of the one-dimension grid size n. Thus, paradoxically, the complexity of the grid-based evaluation of the Coulumb and exchange matrices becomes almost independent of the grid size, being regulated only by the structure of a molecular system. As a result, the grid approximation of the Hartree-Fock equation allows to gain the high resolution with a guaranteed accuracy.

Key words: Tensor-structured methods, QTT format, electronic structure calculations, Hartree-Fock equation, Coloumb and exchange operators.

AMS Subject Classification: 65F30, 65F50, 65N35, 65F10

1 Introduction

The Hartree-Fock equation is a nonlinear eigenvalue problem with the Fock operator incorporating the convolution integrals in $\mathbb{R}^3$, which depend on the eigenfunctions in question. This 3D eigenvalue problem can be solved only iteratively, using the self-consistent field iterations. In view of its dimensionality and in presence of strong cusps in the electron density and molecular orbitals, it presupposes an inherent concept of the separation of variables. This principal background has led to the conventional approaches based on the analytical precomputation of the two-electron integrals requiring the usage of the naturally separable

*The paper was completed during the participation of all the three authors in the HIM Trimester Program "Analysis and Numerics for High Dimensional Problems" (Bonn, 2011).

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basis (Gaussian type basis sets) [17, 34]. In electronic structure calculations, the employment of analytically separable basis functions has a long history [5, 1]. It concerns both the Gaussian-type basis sets, and the plane waves bases, which in spite of intrinsic limitations, are the cornerstone for the DFT calculations [10, 41].

In recent decades, a number of the state-of-the-art program packages have been developed for the solution of the Hartree-Fock equation. Mostly, they are based on the analytical precalculation of the two-electron integrals in the precisely selected Gaussian bases [45, 11], hence requiring a large number of precomputed parameters, which are incorporated as the data sets for certain types of molecules. Furthermore, improving the accuracy by increasing the number of Gaussian type basis functions is limited by the increasing instability of these bases.

Meanwhile, a substantial progress has been achieved in the computer science community on the tensor decomposition techniques in the multilinear algebra via the canonical and the Tucker models, see [6, 33]. Moreover, there are interesting results on the tensor-product approximation of the 3D Newton and Yukawa potentials in the framework of the wavelet- and polynomial-based multiresolution schemes [16, 4], as well as using the grid-based approximations [13, 8, 25, 29].

The rank-structured algorithms of the multilinear algebra based on the Tucker-canonical type approximation applied to the class of function related tensors in $\mathbb{R}^d$, $d \geq 3$, are considered in [24] (see also references therein). Owing to this concept, the grid-based tensor approximation of functions and operators in the Hartree-Fock equation led to efficient tensor numerical algorithms for electronic structure calculations:

- low-rank representation of the Galerkin and collocation discretizations of the Newton and Yukawa convolving kernels [3],
- fast $3D$ (nD) convolution with the Green kernels in $1D$ complexity [25],
- robust multigrid canonical-to-Tucker-to-canonical rank reduction scheme, in $1D$ complexity for $3D$ case [28, 24],
- tensor calculation of the Coulomb and exchange integrals in $\mathbb{R}^3$ by means of a combination of $1D$ Hadamard and scalar products and $1D$ convolutions [30, 23, 24].

We summarize that the main advantage of the multilevel tensor-structured methods is in the "black-box"-type evaluation of the 3D/6D integral operators with the Green's convolving kernels employing the low-rank algebraic separability of the discretized operators and functions in $\mathbb{R}^d$, $d \geq 3$. Another gain of the rank-structured techniques is flexibility in the choice of the grid-based basis functions admitting the separation ranks larger than 1 (say, the Slater-type basis). This approach does not need the analytical precomputation of the two-electron integrals and can be applied to rather general many-electron systems discretized on large tensor grids.

In the present paper we make the next step in the development of the grid-based methods using the rank-structured tensor representation of functions and operators in electronic structure calculations by imposing the so-called quantized tensor representation. Recently introduced quantics-TT (QTT) tensor format [26, 35, 31] provides $O(\log n)$-complexity of the 3D tensor operations, where n is the univariate grid size (see §2 for more detail). Its

application to the problems of computational chemistry leads to paradoxically almost "mesh-independent" grid-based methods. In this paper, we apply the QTT format in the tensor-structured numerical solution of the Hartree-Fock equation [30, 24]. It is shown that the complexity of order $O(\log n)$ is achieved at the most time consuming steps in the tensor calculation of the Coulomb and exchange operators.

The rest of the paper is organized as follows. In Section 2 we recall the operators and functions in the Hartree-Fock equation and outline the tensor methods for its solution. Section 3 describes the basic tensor formats and tensor-structured operations. Section 4 recalls the tensor formulation of the Galerkin problem for the grid-based multilevel numerical solution of the Hartree-Fock equation. It presents the main results of the paper, showing that in the essential parts of the rank-structured evaluation of the Fock operator, the QTT format leads to an almost grid independent complexity bound. We present the numerical experiments for a number of moderate size molecules, where the computations are performed on large 3D tensor grids.

2 The Hartree-Fock equation

One of the important problems in electronic structure calculations is to solve numerically the electronic Schrödinger equation

$$\mathcal{H}\Psi = E\Psi,$$

with the electronic Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_A^M \sum_i^N \frac{Z_A}{\|R_A - r_i\|} + \sum_i^N \sum_{j\neq i}^N \frac{1}{r_{ij}},$$

for a system with M nuclei and N electrons. For the computation of the ground state energy of a many-electron system, one can minimize the energy functional for the electronic Hamiltonian with the antisymmetric Slater determinant wavefunction ansatz. This yields the Hartree-Fock equation (we consider a closed shell system)

$$\mathcal{F}_\Phi \psi_i(x) = \lambda_i \, \psi_i(x), \quad \int_{\mathbb{R}^3} \psi_i \psi_j dx = \delta_{ij}, \; i,j = 1, ..., N \tag{1}$$

which is an eigenvalue problem with respect to the molecular orbitals ψ_i. Here $\mathcal{F}_\Phi$ is a nonlinear Fock operator

$$\mathcal{F}_\Phi := -\frac{1}{2}\Delta + V_c + V_H - \mathcal{K}.$$

with the nuclear potential

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

Here the Hartree potential $V_H(x)$

$$V_H(x) := \int_{\mathbb{R}^3} \frac{\rho(y)}{\|x - y\|} \, dy, \quad x \in \mathbb{R}^3, \tag{2}$$

and the nonlocal exchange operator $\mathcal{K}$

$$(\mathcal{K}\psi)(x) := \frac{1}{2}\int_{\mathbb{R}^3} \frac{\tau(x,y)}{\|x-y\|}\,\psi(y)dy, \tag{3}$$

with the density matrix $\tau(x,y)$, and electron density $\rho(x)$,

$$\tau(x,y) := 2\sum_{a=1}^{N} \psi_a(x)\psi_a(y), \quad \rho(x) := \tau(x,x).$$

are the functions of the desired solution of (1). Thus, due to the nonlinear dependence of the Hartree-Fock equation (1) on its solution, this eigenvalue problem can be solved only iteratively. Mostly, improved modifications of the self-consistent iteration are applied. It is discretized by the standard Galerkin scheme applied to the initial problem in the form (1) posed in $H^1(\mathbb{R}^3)$ [34]. As an established standard, the naturally separable Gaussian basis set $\{g_m\}_{1\le m\le N_b}$ can be used which is well suited for the analytical computation of the arising 3D and 6D integrals. On the other hand, the plane waves and finite element basis sets might be the possible alternative.

Traditionally, the molecular orbitals in the given basis set $\{g_m\}_{1\le m\le N_b}$ are expanded as

$$\psi_a(x) = \sum_{m=1}^{N_b} C_{ma} g_m(x), \quad a = 1, ..., N, \tag{4}$$

implying

$$\tau(x,y) = 2\sum_{a=1}^{N} \psi_a(x)\psi_a(y) = 2\sum_{a=1}^{N} \left(\sum_{m=1}^{N_b} C_{ma} g_m(x)\right)\left(\sum_{m=1}^{N_b} C_{ma} g_m(y)\right),$$

and the respective representation for $\rho(x)$. Consequently, we have

$$V_H(x) = \rho * \frac{1}{\|\cdot\|}(x) = \int_{\mathbb{R}^3} \sum_{a=1}^{N} \frac{\left(\sum\limits_{m=1}^{N_b} C_{ma} g_m(y)\right)^2}{\|x-y\|} dy.$$

In this way, the mass (overlap) matrix $S = \{S_{\mu\nu}\}_{1\le\mu,\nu\le N_b}$, is given by

$$S_{\mu\nu} = \int_{\mathbb{R}^3} g_\mu g_\nu dx.$$

The core Hamiltonian part $H = \{h_{\mu\nu}\}$ of the stiffness matrix $\mathcal{H} = -\frac{1}{2}\Delta + V_c$,

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

includes the kinetic energy of electrons and the nuclear-electron interaction potential.

In the tensor approach [24, 30] the Galerkin Hartree $J(C)$ and exchange $K(C)$ matrices are expressed as

$$J(C)_{\mu\nu} = \int_{\mathbb{R}^3} V_H(x) g_\mu(x) g_\nu(x) dx = \langle V_H, g_\mu g_\nu \rangle_{L^2(\mathbb{R}^3)} \tag{5}$$

and

$$K(C)_{\mu\nu} = -\frac{1}{2}\iint_{\mathbb{R}^3} \frac{\tau(x,y)}{\|x-y\|}\, g_\nu(y) g_\mu(x) dydx \tag{6}$$
$$= -\sum_{a=1}^{N} \iint_{\mathbb{R}^3} \frac{g_\nu(y)\left(\sum_{m=1}^{N_b} C_{ma} g_m(y)\right)}{\|x-y\|} g_\mu(x) \left(\sum_{m=1}^{N_b} C_{ma} g_m(x)\right) dydx,$$

respectively. The complete Fock matrix $F = F(C)$ is then given by

$$F(C) = H + G(C), \quad G(C) = J(C) + K(C). \tag{7}$$

The Galerkin approximation scheme applies to the unknown coefficients matrix $C = \{C_{ma}\} \in \mathbb{R}^{N_b \times n}$. Now the traditional Galerkin system of nonlinear equations for (1) describing the coefficients matrix $C \in \mathbb{R}^{N_b \times n}$, takes the form,

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

where the second equation represents the orthogonality constraints $\int_{\mathbb{R}^3} \psi_i \psi_j = \delta_{ij}$, with I_{N_b} being the $N_b \times N_b$ identity matrix.

This nonlinear eigenvalue problem is solved by the self-consistent field iteration using the standard direct inverse of the iterative subspaces (DIIS) method [39] providing fast local convergence. The Hartree and exchange matrices $J(C)$ and $K(C)$ have to be recomputed at each iterative step.

In our Galerkin scheme the basis functions $\{g_m\}_{1 \le m \le N_b}$ are first represented on fine enough 3D tensor grid required for the resolution of multiple cusps in the electron density. Hence, the key point in the tensor approach is the efficient calculation of 3D and 6D integrals in (5) and (6) by using fast multilinear operations via the grid-based low-rank tensor representation of all potentials and convolution kernels involved. Application of the QTT tensor format, as proposed in this paper, leads to $O(\log n)$ complexity scaling in the univariate grid-size n enabling us the high spatial resolution via the fine mesh.

3 Tensor-structured formats

In this section, for the ease of exposition, we present a short description of the basic additive and multiplicative tensor-structured formats.

Tensor of order d is defined as an element of finite dimensional tensor-product Hilbert space $\mathbb{W}_{\mathbf{n}} \equiv \mathbb{W}_{\mathbf{n},d}$ of the d-fold, $n_1 \times ... \times n_d$ real-valued arrays, and equipped with the Euclidean (Frobenius) scalar product $\langle \cdot, \cdot \rangle : \mathbb{W}_{\mathbf{n}} \times \mathbb{W}_{\mathbf{n}} \to \mathbb{R}$. Each tensor in $\mathbb{W}_{\mathbf{n}}$, $\mathbf{n} = (n_1, ..., n_d)$, can be represented componentwise,

$$\mathbf{A} = [A(i_1, ..., i_d)] \quad \text{with} \quad i_\ell \in I_\ell := \{1, ..., n_\ell\},$$

where for the ease of presentation, we mainly consider the equal-size tensors, i.e., $n_\ell = n$ ($\ell = 1, ..., d$). We call the elements of $\mathbb{W}_{\mathbf{n}} = \mathbb{R}^{I_1 \times ... \times I_d}$ as n-d tensors. Dimension of the

tensor-product Hilbert space $\mathbb{W}_{\mathbf{n}}$ scales exponentially in d, $\dim \mathbb{W}_{\mathbf{n}} = n^d$ implying the exponential storage cost for a general n-d tensor.

The basic additive type separable representations of tensors are described by the so-called canonical and Tucker formats. We say that $\mathbf{A} \in \mathbb{W}_{\mathbf{n}}$ belongs to the rank-R canonical format if

$$A(i_1, \ldots, i_d) = \sum_{\alpha=1}^{R} A^{(1)}(i_1, \alpha) \ldots A^{(d)}(i_d, \alpha), \quad A^{(k)}(\cdot, \alpha) \in \mathbb{R}^{n_k}.$$

Now the storage cost is bounded by dRn. Furthermore, we say that $\mathbf{A} \in \mathbb{V}_{\mathbf{n}}$ belongs to the rank $\mathbf{r} = [r_1, \ldots, r_d]$ Tucker format if

$$A(i_1, \ldots, i_d) = \sum_{\alpha_1, \ldots, \alpha_d = 1}^{\mathbf{r}} G(\alpha_1, \ldots, \alpha_d) A^{(1)}(i_1, \alpha_1) \ldots A^{(d)}(i_d, \alpha_d).$$

In this case the storage cost is estimated by $drn + r^d$.

The matrix product representation of a dth order tensor reduces the complexity of storage to $O(dr^2 n)$, where r is the maximal mode rank, (cf. matrix product states (MPS) in DMRG quantum computations [46, 43, 44]). The matrix product type tensor approximation was proved to be efficient in high-dimensional electronic/molecular structure calculations, in quantum computing and in stochastic PDEs (see the survey publications [27, 42, 20]). In the recent mathematical literature the various versions of matrix product tensor decomposition were discussed as the tensor train (TT) [36, 38], the tensor chain (TC) [26] and the closely related hierarchical Tucker [15] formats. Further reduction of the asymptotic storage complexity was proved to be efficient based on the so-called quantized TT (QTT) representation [26] (see also [35]) obtained by folding of the initial tensor to a higher dimensional $2 \times ... \times 2$ array. In the following we make use of the both TT and QTT formats.

Tensor chain/train formats are defined as follows. For a given rank parameter $\mathbf{r} = (r_0, ..., r_d)$, and the respective index sets $J_\ell = \{1, ..., r_\ell\}$ $(\ell = 0, 1, ..., d)$, with the periodicity constraints $J_0 = J_d$ (i.e., $r_0 = r_d$), the rank-$\mathbf{r}$ TC format contains all elements $\mathbf{A} = [A(i_1, ..., i_d)] \in \mathbb{W}_{\mathbf{n}}$ which can be represented as the chain of contracted products of 3-tensors over the d-fold product index set $J := \times_{\ell=1}^{d} J_\ell$,

$$A(i_1, ..., i_d) = \sum_{\alpha_1 \in J_1} \cdots \sum_{\alpha_d \in J_d} A^{(1)}(\alpha_d, i_1, \alpha_1) A^{(2)}(\alpha_1, i_2, \alpha_2) \cdots A^{(d)}(\alpha_{d-1}, i_d, \alpha_d).$$

In the matrix form we have the entrywise MPS representation

$$A(i_1, i_2, \ldots, i_d) = A^{(1)}_{i_1} A^{(2)}_{i_2} \ldots A^{(d)}_{i_d}, \tag{8}$$

where each $A^{(\ell)}_{i_\ell}$ is $r_{\ell-1} \times r_\ell$ matrix.

In the case $J_0 = J_d = \{1\}$, the TC format coincides with TT representation. The TC/TT format reduces the storage cost of n-d tensor to log-volume size $O(dr^2 n)$, $r = \max r_\ell$.

It was shown in [26] that the computational gain of the QTT representation is due to the fact that a class of discrete exponential (resp. trigonometric) n-vectors allows the rank-1 (resp. TT rank-2) dyadic folding representation, reducing the storage complexity $O(n)$ to the logarithmic bound $O(2 \log_2 n)$; similar result holds for polynomial vectors sampled

over uniform or properly refined grids. The efficient QTT representation for a class of multidimensional operators and potentials was proven in [21, 32]. Moreover, the basic tensor operations like FFT and convolution transform can be performed in $O(2\log_2 n)$ operations either [7, 22].

We suppose that $n = 2^L$ with some $L = 1, 2, ...$ Next definition introduces the folding of n-d tensors into the elements (quantized $2 \times ... \times 2$ tensors) of auxiliary D-dimensional tensor space with $D = d\log_2 n$. The respective binary folding transform of degree $2 \le L$,

$$\mathcal{F}_{d,L} : \mathbb{W}_{\mathbf{n},d} \to \mathbb{W}_{\mathbf{m},dL}, \quad \mathbf{m} = (\mathbf{m}_1, ..., \mathbf{m}_d), \quad \mathbf{m}_\ell = (m_{\ell,1}, ..., m_{\ell,L}),$$

with $m_{\ell,\nu} = 2$ for $\nu = 1, ..., L$, $(\ell = 1, ..., d)$, that reshapes the initial $\mathbf{n}$-d tensor in $\mathbb{W}_{\mathbf{n},d}$ to the elements of tensor product space

$$\mathbb{W}_{\mathbf{n},dL} = \bigotimes_{\ell=1}^{d} \mathbb{K}^{n_\ell} = \bigotimes_{\ell=1}^{d} \bigotimes_{j=1}^{L} \mathbb{K}^2,$$

is defined as follows:
(A) For $d = 1$ a vector $\mathbf{X} = [X(i)]_{i\in I} \in \mathbb{W}_{n,1}$, is reshaped to the element of $\mathbb{W}_{2,L}$ by

$$\mathcal{F}_{1,L} : \mathbf{X} \to \mathbf{Y} = [Y(\mathbf{j})] := [X(i)], \quad \mathbf{j} = \{j_1, ..., j_L\},$$

with $j_\nu \in \{1, 2\}$ for $\nu = 1, ..., L$. For fixed i, $j_\nu = j_\nu(i)$ is defined by $j_\nu - 1 = C_{-1+\nu}$, where the $C_{-1+\nu}$ are found from the binary representation (binary coding) of $i - 1$,

$$i - 1 = C_0 + C_1 2^1 + \cdots + C_{L-1} 2^{L-1} \equiv \sum_{\nu=1}^{L} (j_\nu - 1) 2^{\nu-1}.$$

(B) For $d > 1$ the construction is similar.

Notice that every 2-(dL) tensor in high-dimensional space $\mathbb{W}_{2,dL}$ can be represented (approximated) in the low rank TT format. This leads to the so-called QTT representation of n-d tensors. Assuming that $r_k \le r$, $k = 1, ..., dL$, the complexity of QTT representation can be estimated by $O(dr^2 \log n)$, providing log-volume asymptotics in the size of initial tensor $O(n^d)$.

It is worth to note that the important multilinear algebraic operations with canonical, Tucker and TT tensors can be implemented with linear complexity scaling in n. In particular, for the rank-R_1 and rank-R_2 canonical tensors $\mathbf{X}, \mathbf{Y}$ we have

$$\langle \mathbf{X}, \mathbf{Y} \rangle = \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} \prod_{\ell=1}^{d} \left\langle X^{(\ell)}(\cdot, k), Y^{(\ell)}(\cdot, m) \right\rangle,$$

while the Hadamard product is computed by

$$\mathbf{X} \odot \mathbf{Y} := \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} \left(X^{(1)}(\cdot, k) \odot Y^{(1)}(\cdot, m) \right) \otimes \ldots \otimes \left(X^{(d)}(\cdot, k) \odot Y^{(d)}(\cdot, m) \right).$$

The convolution product of two tensors in the canonical format is given by

$$\mathbf{X} * \mathbf{Y} := \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} \left(X^{(1)}(\cdot, k) * Y^{(1)}(\cdot, m) \right) \otimes \ldots \otimes \left(X^{(d)}(\cdot, k) * Y^{(d)}(\cdot, m) \right), \tag{9}$$

leading to the asymptotic complexity $O(dn \log nR_1R_2)$.

For the Hadamard product in TT format we have

$$\mathbf{Z} = \mathbf{X} \odot \mathbf{Y}: \quad Z^{(k)}(i_k) = X^{(k)}(i_k) \otimes Y^{(k)}(i_k),$$

implying the formatted representation of the scalar product (in $O(dr^3n) \ll n^d$ operations [36])

$$\langle \mathbf{X}, \mathbf{Y} \rangle = \langle \mathbf{X} \odot \mathbf{Y}, \mathbf{1} \rangle.$$

Consequently, the standard multilinear operations like the scalar, Hadamard, contracted and convolution products can be implemented in $O(d \log n)$ operations and storage costs in the quantized-canonical or quantized-TT representations. This allows fast computations on large spacial grids, where n is usually associated with the univariate grid size.

4 Tensor-structured evaluation of the Hartree and exchange operators

4.1 Discretization on tensor grid

As it was mentioned, the tensor-structured numerical calculation of the Hartree and exchange operators [30, 24] does not require the analytical precomputation of the two-electron integrals. Instead, the evaluation of the 3D and 6D convolution integrals (2) and (5) is substituted by a combination of the univariate convolutions, Hadamard and scalar products leading to $1D$ complexity. Hence, the corresponding tensor operations are carried out using fast multilinear algebra in the canonical and Tucker formats supplemented by the corresponding rank optimization (tensor truncation) using the robust canonical-to-Tucker-to-canonical transform.

Here, we combine the canonical, Tucker and ultimately, the QTT formats for fast computation of the Coulomb (5) and exchange (6) matrices which requires tensor evaluation of $N_b(N_b+1)/2$ matrix elements.

We suppose that the initial problem is posed in the finite volume box $\Omega = [-b, b]^3 \in \mathbb{R}^3$ subject to the homogeneous Dirichlet boundary conditions on $\partial\Omega$. For given discretization parameter $n \in \mathbb{N}$, introduce the equidistant tensor grid $\omega_{\mathbf{3},n}$ with the mesh-size $h = 2b/n$. Then define the set of piecewise constant basis functions $\{\phi_{\mathbf{i}}\}$, $\mathbf{i} \in \mathcal{I} := \{1, ..., n\}^3$, associated with the respective grid-cells in $\omega_{\mathbf{3},n}$ (indicator functions), and introduce the set of collocation discretization of GTO basis functions, $\{\overline{g}_k\}$, represented in this basis by the rank-1 coefficients tensor $\{\mathbf{G}_k\} \in \mathbb{R}^{\mathcal{I}}$ $(k = 1, ..., N_b)$. Note that we use the discretized Gaussians $\{\overline{g}_k\}$ for the ease of the comparison of the results with the benchmark package MOLPRO [45]. Our approach is applicable for rather general grid-based basis sets with low tensor ranks.

The projected Newton potential is accurately represented in basis set $\{\phi_{\mathbf{i}}\}$ by the low-rank canonical tensor $\mathbf{P}_N \in \mathbb{R}^{\mathcal{I}}$, see [3].

For the numerical calculations of the Hartree and exchange operators in tensor format we apply the MATLAB package developed by V. Khoromskaia [24]. For fast computation of scalar products (with almost grid independent complexity scaling) we then apply the QTT

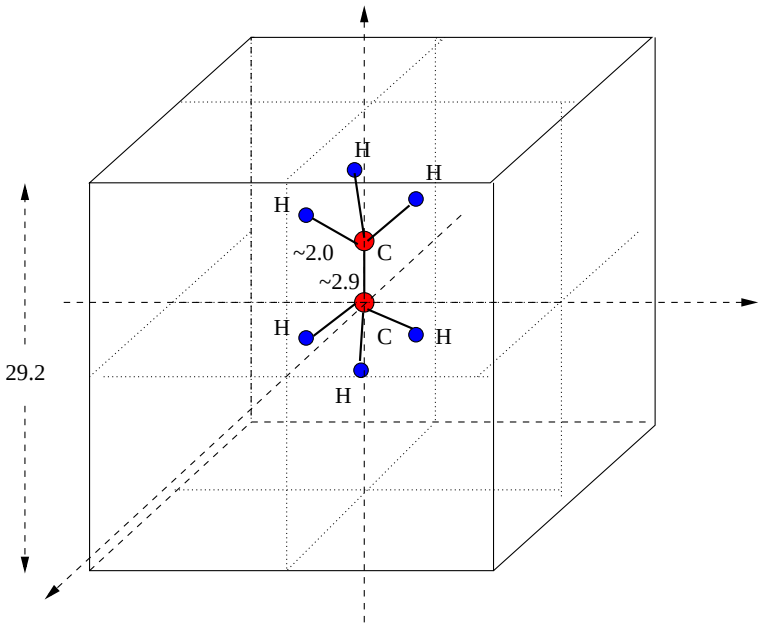

Figure 1: The finite volume box $\Omega = [-b, b]^3 \in \mathbb{R}^3$, $b = 14.6$ au for the C_2H_6 molecule.

tensor format by using the respective subroutines in the MATLAB TT-Toolbox (I. Oseledets, S. Dolgov, http://github.com/oseledets/TT-Toolbox). Here, the practical use of the QTT operations requires the preliminary multigrid rank reduction algorithms from [24].

4.2 Computation of the Coulomb matrix

The tensor-structured computational scheme for the Coulomb matrix (5) can be written by the following tensor operations [30, 24]. First, represent the electron density by a low-rank canonical tensor:

$$\rho \approx \boldsymbol{\rho} := \sum_{a=1}^{N_{orb}} \left(\sum_{\kappa,\lambda=1}^{N_b} c_{\kappa a} c_{\lambda a} \mathbf{G}_\kappa \odot \mathbf{G}_\lambda \right),$$

and then compute the Hartree potential by the tensor-product convolution [25]

$$V_H = \rho * \frac{1}{\|\cdot\|} \approx \boldsymbol{\rho} * \mathbf{P}_N, \tag{10}$$

with $\mathbf{P}_N \in \mathbb{W}_n$ being the projection tensor for the Newton potential. Then the tensor representation of the Coulomb matrix in (5) is obtained by

$$J(C)_{\mu\nu} = \langle \overline{g}_\mu(x) \overline{g}_\nu(x), V_H(x) \rangle \approx \langle \mathbf{G}_\mu \odot \mathbf{G}_\nu, \boldsymbol{\rho} * \mathbf{P}_N \rangle, \quad 1 \le \mu, \nu \le N_b. \tag{11}$$

Here the canonical $rank(\mathbf{G}_\mu) = 1$, while 3rd order tensors $\boldsymbol{\rho}$ and $\mathbf{P}_N$ are approximated by low-rank tensors. Here, we supplement the evaluation of the Coulomb matrix by further QTT data compression techniques, thus performing the following steps:

- Hadamard products of discretized Gaussians to generate electron density tensor $\boldsymbol{\rho}$.

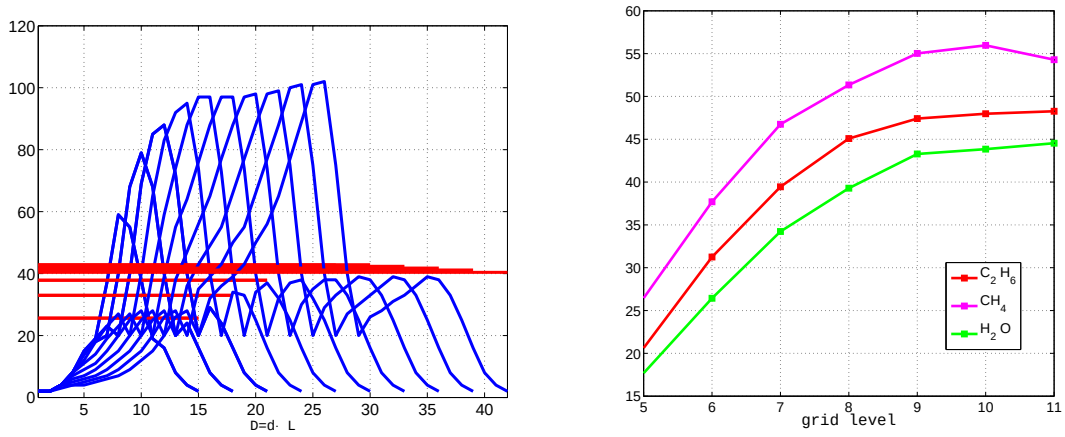

Figure 2: QTT ranks of the Hartree potential (blue lines) and the average QTT rank $\overline{r}_{QTT}$ (red) for CH_4 (left). Average ranks of the QTT cores for CH_4, C_2H_6, H_2O vs. the levels L of the one-dimension grid size $n = 2^L$ (right).

- MG canonical-to-Tucker rank reduction for the density tensor $\boldsymbol{\rho}$ [28].
- Compute $\boldsymbol{\rho} * \mathbf{P}_N$ in the canonical format, by the tensor-product convolution [25].
- MG canonical-to-Tucker-to-canonical rank reduction to represent the Hartree potential V_H (note that the QTT decomposition algorithms cannot be applied directly due to large-ranks tensor $\boldsymbol{\rho} * \mathbf{P}_N$).
- Make the TT and QTT representation of the rank-optimized tensors $\boldsymbol{\rho} * \mathbf{P}_N$ and $\mathbf{G}_\mu \odot \mathbf{G}_\nu$.
- Calculate the Coulomb matrix by the scalar products in the QTT format.

Figure 2 (left) and Figure 4 represent QTT ranks of the optimized tensor $\boldsymbol{\rho} * \mathbf{P}_N$ (accuracy 10^{-6}) for the CH_4, C_2H_6 and H_2O molecules vs. the number of the QTT cores which depends logarithmically on the grid size. We use the grids with $n^3 = 2^{3L}$, $L \le 14$ for CH_4, and $L = 11$ for H_2O and C_2H_6, with the number of the QTT cores $D = dL = 3L$, for $d = 3$. The red line here corresponds to the average QTT rank for the corresponding grid size, given by

$$\overline{r}_{QTT} = \sqrt{\frac{1}{D}\sum_{k=0}^{D-1} r_k r_{k+1}}, \quad D = 3L.$$

Since the QTT ranks are not uniformly distributed, the ranks in the "middle" modes appear to be much larger than at the border modes. With this notation the storage cost of the QTT-tensor is bounded by (in our application $d = 3$)

$$Stor(\mathbf{A}) \le 2\, d\, \overline{r}_{QTT}^2 \log n.$$

Figure 3 shows the times for the QTT (blue line) format in comparison with the canonical

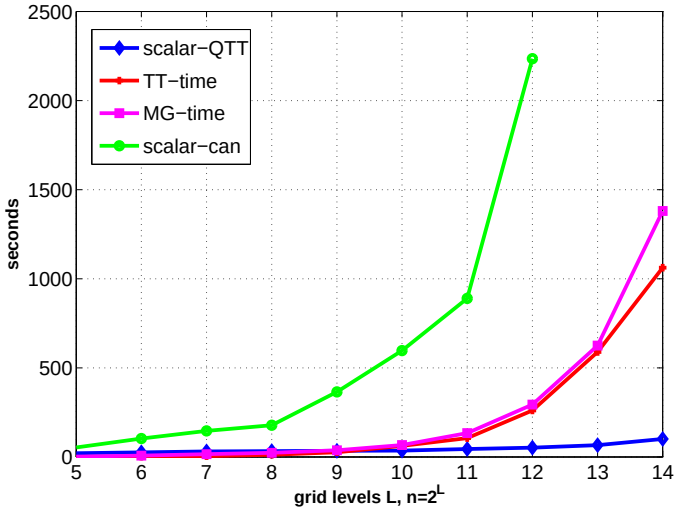

Figure 3: Times for 3D computations vs. the levels L of the one-dimension grid size $n = 2^L$ in the calculation of the Coulomb operator for CH_4. The maximum grid size is $n^3 = 2^{42} \approx 10^{12}$.

format computation (green line) of the Coulomb matrix for CH_4. The red line displays the time for the necessary step of the multigrid accelerated rank reduction [28] preceding to the TT-QTT transforms. Notice that the canonical computation of the Hartree potential V_H yields the canonical tensor of the initial rank $\approx 10^4$, which is not tractable for the TT-QTT transform. The MG rank optimization reduces the canonical rank to $\approx 10^2$, then we apply the TT-QTT transforms. Here the TT transform also scales linearly in the grid size n, see (magenta) line "TT-time" in Figure 3 (right). The "Coulomb-can" (green) line in Figure 3 shows the computational time for the Coulomb matrix without reduction of the rank of V_H, which is not shown for the grids with $n > 2^{12}$ ($L > 12$). The maximum one-dimension grid size of all the other computations presented in Figure 3 attains $n = 2^{14}$, which corresponds to a volume size with huge number of entries $n^3 = 2^{14*3} \approx 10^{12}$.

4.3 Computation of the exchange matrix

The exchange matrix $K(C)$ is computed in three steps, see [23, 24]. For $a = 1, ..., N_{orb}$, and $\nu = 1, ..., N_b$, compute the convolution integrals,

$$W_{a\nu}(x) = \int_{\mathbb{R}^3} \frac{\overline{g}_\nu(y) \sum_{m=1}^{N_b} c_{ma}\overline{g}_m(y)}{\|x-y\|} dy \approx \boldsymbol{W}_{a\nu} := \left[\mathbf{G}_\nu \odot \sum_{m=1}^{N_b} c_{ma}\mathbf{G}_m\right] * \mathbf{P}_N, \qquad (12)$$

and then the scalar products $(\mu, \nu = 1, ..., N_b)$,

$$K_{\mu\nu,a} = \int_{\mathbb{R}^3} \left[\sum_{m=1}^{N_b} c_{ma}\overline{g}_m(x)\right] \overline{g}_\mu(x) W_{a\nu}(x) dx \approx \boldsymbol{K}_{\mu\nu,a} := \langle \mathbf{G}_\mu \odot \left[\sum_{m=1}^{N_b} c_{ma}\mathbf{G}_m\right], \boldsymbol{W}_{a\nu}\rangle. \quad (13)$$

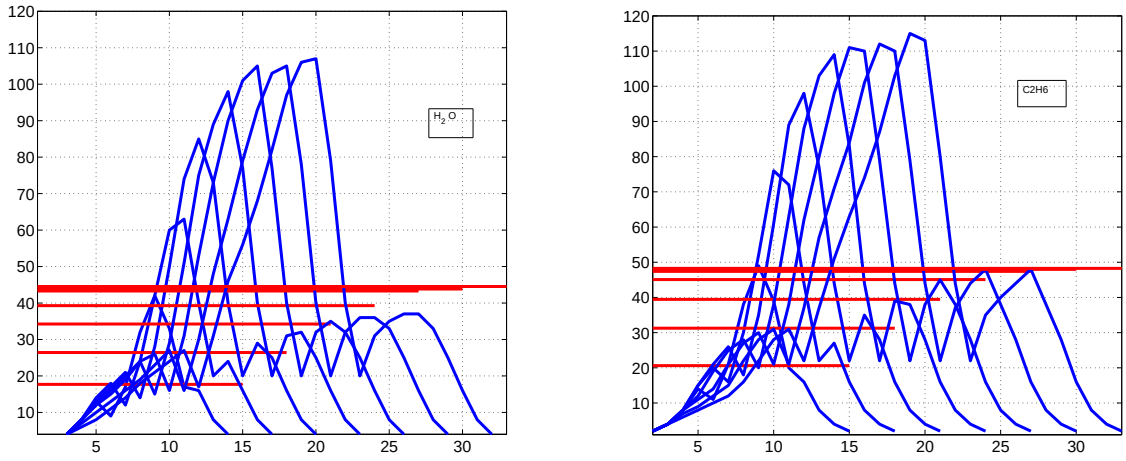

Figure 4: QTT ranks of V_H for all electron case of H_2O (left) and C_2H_6 (right).

Finally, the entries of the exchange matrix are given by sums over all orbitals,

$$K(C)_{\mu\nu} = \sum_{a=1}^{N_{orb}} K_{\mu\nu,a}, \quad \mu,\nu = 1,...,N_b. \tag{14}$$

This scheme gains from the low-rank separable approximation of the Newton kernel, the discretized electron density $\rho(x)$, and of auxiliary potentials $W_{a\nu}(x)$ at step (12), that ensures low complexity of the three-dimensional tensor-structured operations including the rank reduction algorithms.

Again, as for the Coulomb matrix, we compute the time consuming N_b^2 scalar products in the QTT format. Thus yielding the following steps in the evaluation of the one orbital contribution of the exchange matrix:

- Compute the convolution integrals $\boldsymbol{W}_{a\mu}$ in the canonical format (see [23]).
- Reduce the canonical rank of $\boldsymbol{W}_{a\mu}$ by using the canonical-to-Tucker and Tucker-to-canonical transforms.
- Represent the canonical tensors $\boldsymbol{W}_{a\mu}$ and $\mathbf{G}_\mu \odot \sum_{m=1}^{N_b} c_{ma}\mathbf{G}_m$ in TT and QTT formats.
- Compute the entries of the exchange matrix as scalar products (13) in QTT format.

Figure 5 represents average QTT ranks of the Gaussians (Hadamard products $\mathbf{G}_\kappa \odot \mathbf{G}_\lambda$) vs. one-dimension grid-size n, $\varepsilon = 10^{-6}$ (left) and vs. ε, $n = 1024$ (right), in the case of CH_4 molecule. It is clearly seen that the average QTT ranks are almost uniformly bounded in n and depend logarithmically on the approximation accuracy ε.

Figure 6 gives the examples of QTT ranks in the computation of the exchange potential for H_2O. QTT ranks of tensors $\boldsymbol{W}_{a\mu}$ (left) and $\mathbf{G}_\mu \odot \sum_{m=1}^{N_b} c_{ma}\mathbf{G}_m$ (right) are given for the

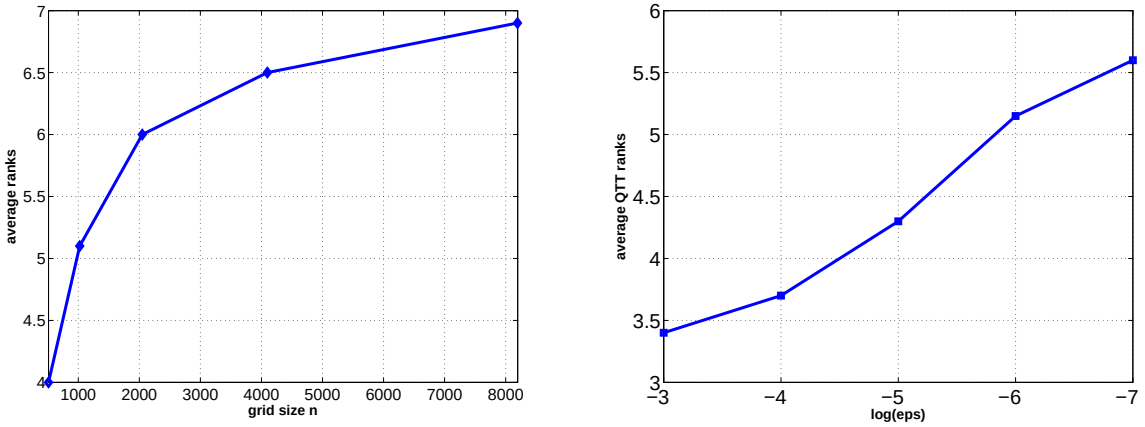

Figure 5: Average QTT ranks of the 3D Gaussians (Hadamard products $\mathbf{G}_\kappa \odot \mathbf{G}_\lambda$) vs. 1D grid-size n, $\varepsilon = 10^{-6}$ (left) and vs. ε, $n = 1024$ (right).

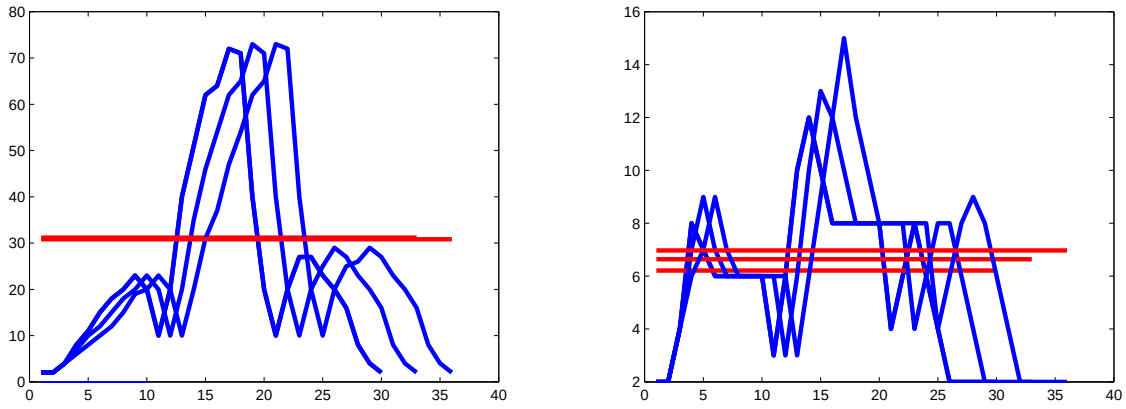

Figure 6: Examples of the QTT ranks of the exchange potential for H_2O: Tensors $\boldsymbol{W}_{a\mu}$ (left) and $\mathbf{G}_\mu \odot \sum_{m=1}^{N_b} c_{ma}\mathbf{G}_m$ (right).

grid size $n = 2^L$, $L = 10, 11, 12$. It is easily seen that the averaged QTT cores ranks for these tensors are almost independent on the grid size n.

5 Conclusions

The tensor-structured numerical evaluation of the Coulomb and exchange operators in the Hartree-Fock equation is supplemented by the usage of the QTT format, leading to $O(\log n)$ complexity represention of the respective 3D convolution integrals discretized on the large $n \times n \times n$ Cartesian grid.

We demonstrate that the QTT ranks of the discretized Hartree and exchange potentials are nearly independent of the one-dimension grid-size n. Hence, the complexity of the 3D grid-based tensor operations for evaluation of the Coulomb and exchange matrices, $J(C)$ and $K(C)$, becomes almost independent on n, being regulated only by the tensor ranks characterising the topology of a molecular system. We present numerical illustrations of the QTT approximation to the Hartree and exchange integral operators of some moderate size molecules for the grid-size in the range $n \leq 2^{14}$.

Our results demonstrate that the grid-based QTT tensor-structured solution of the Hartree-Fock equation (taking into account [22]) can be realized on large 3D grids thus providing a guaranteed precision.

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