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Boris N. Khoromskij, Venera Khoromskaia, and Heinz-Jürgen Flad

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Numerical solution of the Hartree-Fock equation in multilevel tensor-structured format

B.N. Khoromskij[a], V. Khoromskaia[a] and H.-J. Flad[b]
[a] Max-Planck-Institute for Mathematics in the Sciences,
Inselstr. 22-26, D-04103 Leipzig, Germany.
[b] TU Berlin, Strasse des 17.Juni 136, D-10623 Berlin, Germany.
{bokh, vekh, flad}@mis.mpg.de

Abstract

In this paper, we describe a novel method for robust and accurate iterative solution of the self-consistent Hartree-Fock equation in $\mathbb{R}^3$ based on the idea of tensor-structured computation of the electron density and the nonlinear Hartree and (nonlocal) Hartree-Fock exchange operators at all steps of the iterative process. We apply the self-consistent field (SCF) iteration to the Galerkin discretisation in a set of low separation rank basis functions that are solely specified by the respective values on the 3D Cartesian grid. The approximation error is estimated by $O(h^3)$, where $h = O(n^{-1})$ is the mesh size of $n \times n \times n$ tensor grid, while the numerical complexity to compute the Galerkin matrices scales linearly in n. We propose the tensor-truncated version of the SCF iteration using the traditional direct inversion in the iterative subspace (DIIS) scheme enhanced by the multilevel acceleration with the grid dependent termination criteria at each discretization level. This implies that the overall computational cost scales linearly in the univariate problem size n. Various numerical illustrations are presented for the all electron case of H_2O, and pseudopotential case of CH_4 and CH_3OH molecules. The proposed scheme is not restricted to *a priori* given analytically integrable and/or rank-1 basis sets, that opens further perspectives for promotion of the tensor-structured methods in computational quantum chemistry.

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1 Introduction

In the recent years the concept of tensor-structured numerical methods has opened new perspectives for solving the basic equations of mathematical physics in $\mathbb{R}^d$, $d \geq 3$, in particular, the many-particle Schrödinger equation [1, 11, 2, 27], and multidimensional elliptic spectral problems [13, 21]. Tensor methods are based on the idea of separable approximation of d-variate functions and related operators arising in the discretisation and solution process

posed in a multivariate function space in $\mathbb{R}^d$. This concept appears to be particularly attractive for the simplified approaches, like the *ab initio* Hartree-Fock and density functional theory methods reducing the dimensionality of the problem to $d = 3$, though the kernels of the nonlocal operators involved are functions of six spatial dimensions.

The traditional numerical methods in *ab initio* electronic structure calculations are based on the Galerkin approximation in the problem-dependent Gaussian-type orbitals (GTO) basis (meshless methods). Many efforts have been devoted to the development of rigorous schemes for the analytical evaluation of the two- and four-electron integrals inherent for this approach, which yielded state-of-the-art existing packages. The Hartree-Fock model presupposes at least cubic (or fourfold) scaling in the number of the basis functions, thus making computations using the Gaussian bases rapidly increasing for large molecules, troublesome. The simplified models based on the appropriately adjusted pseudopotentials, can be solved by using the grid-oriented methods over $n \times n \times n$ spacial grid via the traditional plane waves, wavelet or finite element discretizations at the expense that scales at least linear in the volume size, $N_V = n^3$, [9, 10]. In this way, the practically tractable grid-size for the calculations using these traditional approaches is limited by the value $n \approx 500$.

The principal question then arises: is it possible to solve the Hartree-Fock/Kohn-Sham models by the grid-based methods with linear scaling in the univariate grid-size n (i.e., sublinear in the volume, $O(N_V^{1/3})$)? In what follows, we give the promising answer to this question by introducing the tensor-structured numerical scheme that solves the Hartree-Fock equation with $O(n)$-complexity. To that end, we introduce the novel concept for the numerical solution of the Hartree-Fock equation which is based on the use of a moderate number of the problem-adapted discrete Galerkin basis functions living on 3D Cartesian grid, and represented with a low separation rank ("global super-elements"). Such a basis can be viewed as a kind of algebraic generalization/optimisation of the traditional GTO or Slater-type orbitals providing the way to $O(n)$ discrete evaluation of the various six-dimensional volume integrals.

The core of our method is the tensor-structured computation of the electron density and the Galerkin matrices of the nonlinear Hartree and (nonlocal) Hartree-Fock exchange operators at all steps of iterations on nonlinearity, based on the systematic use of the rank-truncated linear tensor operations [23, 24, 17]. Within the solution process, all principal multilinear algebra operations, such as the scalar and Hadamard products, the laborious 3D convolution transform, and the rank truncation procedures are implemented with $O(n)$-complexity. Due to linear scaling in n of the 3D tensor-structured arithmetics, we achieve high accuracy of calculations due to accessibility of the large $n \times n \times n$ tensor grids of size up to 16384^3 at the finest approximation level. In electronic structure calculations this implies rather fine resolution with the mesh size $h \approx 10^{-4}$ $\overset{\circ}{A}$ providing possibility for arbitrary space orientation of a molecule in the computational box, as in the case of meshless methods.

Particularly, the *self-consistent field* (SCF) iteration applies to the Galerkin discretisation of the Hartree-Fock equation with respect to certain low separation rank "super-basis". Making use of piecewise linear grid representation of the Galerkin basis functions, and piecewise constant representation of the electron density, leads to the approximation error of order $O(h^2)$, in the Hartree and exchange potentials, where $h = O(n^{-1})$ is the respective mesh size. In turn, the two-grid version of the algorithm improves the convergence rate up to $O(h^3)$. In the case of only few spacial singularities, the locally refined tensor grids can be

adapted.

In this paper the SCF iteration is the traditional *direct inversion in the iterative subspace* (DIIS) scheme commonly used in the physical literature [30, 15, 3]. We propose the enhanced DIIS iteration by the multigrid acceleration with the grid dependent termination criteria at each discretization level. It has the two-fold effect, providing good initial guess on finer grids, and allowing the improved approximation $O(h^3)$, via the Richardson extrapolation over a sequence of grids. We update the discrete orbitals, represented by the respective coefficients vectors, by diagonalising the Galerkin stiffness matrix at each iteration on nonlinearity at the expence $O(N_b^3)$, where N_b is the dimension of the Galerkin subspace. In general, the convergence proof for the nonlinear DIIS iteration is still an open question [26]. We observe that in numerical practice, our multigrid accelerated DIIS iteration exhibits fast and uniform in n convergence (linear convergence rate) so that the overall computational time scales linearly in n—the tool apparently works. It is worth to note that the current version of our method still scales cubically in the size of approximating basis. Hence, any *algebraic optimisation of this basis set* within the solution process gives the new opportunity to high accuracy *ab initio* computations for large molecules. The quadratic scaling in the size of approximating basis might be possible for iterative solving of the Galerkin spectral problem, or in the framework of direct minimization algorithms (see [32] for detailed discussion on the direct minimization).

We present numerical illustrations for the all electron case of H_2O, and pseudopotential cases of the CH_4 and CH_3OH molecules using the particular Galerkin basis set via discretized GTO basis functions. GTO basis is chosen only for the reasons of convenient comparison with the standart MOLPRO package based on the analytical evaluation of the arising integrals [34]. Numerical computations confirm the linear scaling in the grid-size n, indicating the attractive features of the tensor-structured SCF iteration in the prospects of efficient *ab initio* and DFT computations for large molecules.

The rest of the paper is organised as follows. In §2 we describe the standard Galerkin scheme for the nonlinear Hartree-Fock equation, and discuss various types of commonly used sets of Galerkin basis functions. Our choice can be only constrained by the requirements on the low separation rank of the individual basis functions and possibly low dimension of the Galerkin subspace. In §2.3, we introduce the nonstandard agglomerated representations of the Coulomb and Hartree-Fock exchange Galerkin matrices, which are well suited for tensor arithmetics. §2.5 describes the basic representation of the Fock operator in the rank-structured tensor format, that is the key point for efficient $O(n)$-implementation of the tensor-truncated SCF iteration. In §3, we first formulate the SCF iteration that implements the unigrid tensor-truncated DIIS iteration. The (cascadic) multigrid version of the tensor-truncated DIIS iteration includes the Richardson extrapolation over the pair of sequential grids. We prove the $O(N_b^3 n)$-complexity of the proposed numerical method. In the particular case of GTO basis, N_b is proportional to the number of electrons in the molecule. §4 presents various numerical illustrations in the case of moderate-size molecules which confirm the theoretical prediction on $O(n)$-complexity. In §5 the main conclusions are formulated. Appendix gives the description of tensor-structured formats being used in our computational scheme.

2 Galerkin scheme and tensor approximation

2.1 Problem setting

We introduce the tensor-truncated numerical method to compute valuable quantities in the $2N$-electrons Hartree-Fock equation for pairwise L^2-orthogonal electronic orbitals $\psi_i : \mathbb{R}^3 \to \mathbb{R}$, $\psi_i \in H^1(\mathbb{R}^3)$, that reads as

$$\mathcal{F}_\Phi \psi_i(x) = \lambda_i \psi_i(x), \quad \int_{\mathbb{R}^3} \psi_i \psi_j dx = \delta_{ij}, \ i,j = 1,...,N \tag{2.1}$$

with $\mathcal{F}_\Phi$ being the nonlinear Fock operator

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

Here we use the definitions

$$\tau(x,y) := 2\sum_{i=1}^{N} \psi_i(x)\psi_i(y), \quad \rho(x) := \tau(x,x),$$

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

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

for the nuclea potential. The Hartree potential $V_H(x)$ is given by

$$V_H(x) := \rho \star \frac{1}{\|\cdot\|} = \int_{\mathbb{R}^3} \frac{\rho(y)}{\|x-y\|}\, dy, \quad x \in \mathbb{R}^3, \tag{2.2}$$

while the nonlocal exchange operator $\mathcal{K}$ reads as

$$(\mathcal{K}\psi)(x) := -\sum_{i=1}^{N} \left(\psi\, \psi_i \star \frac{1}{\|\cdot\|} \right) \psi_i^*(x) = -\frac{1}{2} \int_{\mathbb{R}^3} \frac{\tau(x,y)}{\|x-y\|}\, \psi(y) dy. \tag{2.3}$$

2.2 Standard Galerkin scheme

We use the standard Galerkin approximation of the initial problem (2.1) posed in $H^1(\mathbb{R}^3)$ (see [26] for more details). For a given finite basis set $\{g_\mu\}_{1\le\mu\le N_b}$, $g_\mu \in H^1(\mathbb{R}^3)$, we expand (approximately) the molecular orbitals ψ_i as

$$\psi_i = \sum_{\mu=1}^{N_b} C_{\mu i} g_\mu, \quad i = 1,...,N. \tag{2.4}$$

To derive the equation for the unknown coefficients matrix $C = \{C_{\mu i}\} \in \mathbb{R}^{N_b \times N}$, we first introduce the mass (overlap) matrix $S = \{S_{\mu\nu}\}_{1\le\mu,\nu\le N_b}$, given by

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

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

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

and the symmetric density matrix

$$D = 2CC^* \in \mathbb{R}^{N_b \times N_b}. \tag{2.5}$$

The nonlinear terms representing the Galerkin approximation of the Hartree and exchange operators are usually constructed by using the so-called two-electron integrals, defined as

$$b_{\mu\nu,\kappa\lambda} = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{g_\mu(x) g_\nu(x) g_\kappa(y) g_\lambda(y)}{\|x-y\|} dxdy, \quad 1 \le \mu, \nu, \kappa, \lambda \le N_b.$$

Introducing the $N_b \times N_b$ matrices $J(D)$ and $K(D)$, with D defined by (2.5),

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

and then the complete Fock matrix F,

$$F(C) = H + G(D), \quad G(D) = G(C) = J(D) + K(D), \tag{2.6}$$

we arrive at the respective Galerkin system of nonlinear equations for the coefficients matrix $C\mathbb{R}^{N_b \times N}$,

$$\begin{aligned} F(CC^*)C &= SC\Lambda, \quad \Lambda = diag(\lambda_1, ..., \lambda_N), \\ C^*SC &= I_N, \end{aligned} \tag{2.7}$$

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

In the standard implementation based on the precomputed two-electron integrals, the complexity to build up the matrix G scales as $O(N_b^4)$, that is dominated by computational cost for the exchange matrix $K(D)$. In turn, the core Hamiltonian H can be precomputed in $O(N_b^2)$ operations, hence, in the following, we will not focus on this issue.

The nonlinear system (2.7) can be solved by certain SCF iteration, where at each iterative step the respective linear eigenvalue problem has to be solved with the updated matrix $G(D)$. Given $F(C)$, using the direct diagonalization for solving the system (2.7) leads to the cost $O(N_b^3)$. The alternative approach can be based on the direct minimization of the Hartree-Fock energy functional,

$$I^{HF} = \inf\left\{ \frac{1}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3} |\nabla\psi_i|^2 + \int_{\mathbb{R}^3} \rho V_c + \frac{1}{2}\int\int_{\mathbb{R}^3} \frac{\rho(x)\rho(y) - |\tau(x,y)|^2}{\|x-y\|} dxdy \right\},$$

under the orthogonality constraints in (2.1), see [32] for more details.

2.3 Agglomerated representation of the Galerkin matrices

In the present approach, the fast and accurate evaluation of the Galerkin matrices $J(D)$ and $K(D)$ is based on certain reorganisation of the standard computational scheme given in §2.2. Specifically, instead of precomputing the full set of two-electron integrals $b_{\mu\nu,\kappa\lambda}$ and the elements of the density matrix D, we use agglomerated representations for $J(D) = J(C)$ and $K(D) = K(C)$. In particular, the Galerkin representation of the Hartree operator (the Coloumb matrix) is now based on the agglomerated integrals,

$$J(C)_{\mu\nu} = \int_{\mathbb{R}^3} g_\mu(x) V_H(x) g_\nu(x) dx, \quad 1 \le \mu, \nu \le N_b, \tag{2.8}$$

including a single convolution transform in $\mathbb{R}^3$ to compute the Hartree potential in (2.2),

$$V_H = \rho * \frac{1}{\|\cdot\|},$$

where the electron density is given by

$$\rho(y) = \sum_{a=1}^{N} \left(\sum_{\kappa,\lambda=1}^{N_b} C_{\kappa a} C_{\lambda a} g_\kappa(y) g_\lambda(y) \right). \tag{2.9}$$

In turn, as proposed in [17], we represent the matrix entries of $K(C)$ by the following three loops: For $a = 1, ..., N$, compute the convolution integrals,

$$W_{a\nu}(x) = \int_{\mathbb{R}^3} \frac{g_\nu(y) \sum\limits_{m=1}^{N_b} C_{ma} g_m(y)}{\|x - y\|} dy, \quad \nu = 1, ..., N_b, \tag{2.10}$$

and then the scalar products

$$K_{\mu\nu,a} = \int_{\mathbb{R}^3} \left[\sum_{m=1}^{N_b} C_{ma} g_m(x) \right] g_\mu(x) W_{a\nu}(x) dx, \quad \mu, \nu = 1, ..., N_b. \tag{2.11}$$

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

$$K(C)_{\mu\nu} = \sum_{a=1}^{N} K_{\mu\nu,a}, \quad \mu, \nu = 1, ..., N_b. \tag{2.12}$$

The advantage of above representations is due to the minimization of the number of convolution products that have to be computed by numerical quadratures. What is even more important, that we have the possibility of efficient low-rank separable approximation of the discretised density $\rho(x)$ as well as of the auxiliary potentials $W_{a\nu}(x)$ at step (2.10).

Effective realization of such a concept is based on certain unrestrictive technical assumptions on the Galerkin basis functions g_μ. First, 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 $\partial\Omega$ (due to the exponential decay of the orbitals $\psi_i(x)$, as $\|x\| \to \infty$). For given discretization parameter $n \in \mathbb{N}$, introduce the equidistant tensor grid

$$\omega_{\mathbf{3},n} := \omega_1 \times \omega_2 \times \omega_3, \quad \omega_\ell := \{-b + (m-1)h : m = 1, ..., n+1\}, \quad \ell = 1, ..., 3, \qquad (2.13)$$

with the mesh-size $h = 2b/n$. 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 the corresponding set $\{\chi_{\mathbf{j}}\}$, $\mathbf{j} \in \mathcal{J} := \{1, ..., n-1\}^3$, of tensor-product continuous piecewise linear (in each spacial variable) polynomials. We denote the corresponding FE spaces as

$$\mathcal{V}_n = \text{span}\{\phi_{\mathbf{i}}\}, \quad \text{and} \quad \mathcal{W}_n = \text{span}\{\chi_{\mathbf{j}}\} \in H_0^1(\Omega).$$

Now the basis set $\{g_\mu\}$ is supposed to satisfy the following properties:

(A) (Approximability). The Galerkin approximation error over the quantities in (2.7) is physically admissible.

(B) (Separability). Each basis function $g_\mu(x) \in H_0^1(\Omega)$, can be represented by the R_G-term separable expansion in $x = (x_1, x_2, x_3)$, with moderate number of terms R_G,

$$g_\mu(x) = \sum_{k=1}^{R_G} g_{\mu,k}^{(1)}(x_1) g_{\mu,k}^{(2)}(x_2) g_{\mu,k}^{(3)}(x_3), \quad \mu = 1, ..., N_b. \qquad (2.14)$$

(C) (Discrete separability). Functions $g_\mu(x)$ allow the approximate representation in either basis sets $\{\phi_{\mathbf{i}}\}$ and $\{\chi_{\mathbf{j}}\}$, by the rank-R_G coefficients tensors $G_\mu = [G_{\mu,\mathbf{i}}] \in \mathbb{R}^{\mathcal{I}}$ and $X_\mu = [X_{\mu,\mathbf{j}}] \in \mathbb{R}^{\mathcal{J}}$, respectively.

(D) (Separable quandratures). The Galerkin integrals for $J(D)$ and $K(D)$ given by (2.8) - (2.12) can be accurately represented by the well separable numerical quadratures in the discrete basis sets $\{G_\mu\}$ and $\{X_\mu\}$, providing asymptotical convergence as $h \to 0$.

Notice that the basis sets $\{\phi_{\mathbf{i}}\}$ and $\{\chi_{\mathbf{j}}\}$ can be generalised to those based on the higher order piecewise polynomials over nonuniform (locally refined) tensor grids. This will only concern with the technical aspects of our approach. The particular numerical effects of such generalisations should be carefully verified on realistic data in electronic structure calculation.

2.4 On the choice of the Galerkin basis functions

The examples of *problem-independent* grid-oriented basis sets are given by plane waves, wavelets, and by the piecewise polynomial *finite element* (FE) basis functions already mentioned in Introduction. Usually, the dimension of the respective Galerkin spaces is much larger than in the case of problem dependent basis sets (see below). The practically tractable grids (indices) of size $n \times n \times n$ are limited by the value $n \approx 500$.

Several efficient "meshless" basis sets $\{g_\mu\}$ are known in the literature on computational quantum chemistry. In particular, we mention the *linear combination of atomic orbitals* (LCAO) and their successors, *Slater-type orbitals* (STOs). The most popular are the so-called *Gaussian-type orbitals* (GTOs) and their more general version, *contracted Gaussian*

functions, which probably constitute the best compromise between STOs and GTOs (cf. [26] for detailed discussion). The construction of such *problem dependent* basis sets is distinctively based on the precomputed electronic orbitals for single atoms.

An alternative to the analytically given GTO-type basis functions are the so-called *fully numerical atomic orbitals* [26], that are solely specified by their numerical values on a grid. Such a choice of basis functions fits well the spirit of our tensor-structured numerical method. On the one hand, this allows to utilise the already existing problem adapted basis sets taking advantage of the important physical information, that is well known for the individual atoms. At this step, in the present approach, one has the possibility to further algebraic optimization of the Galerkin subspace (reduction of the Galerkin dimension N_b). On the other hand, the (low-rank) separable representation of functions and operators reduces the 3D calculations to fast numerical operations implemented only on the univariate grids (1D calculations). In this way, the computation of the volume integrals, convolution transforms, scalar products and function-function multiplications can be simplified dramatically.

The particular requirements on the approximating basis set to be fulfilled in the framework of our tensor-structured numerical scheme are formulated in the previous section (see conditions (A)-(D) in §2.3). The systematic construction of the high-quality low tensor rank approximating basis can be established on:

- Algebraic optimization of the conventional 'meshless" GTO-type basis sets ($R_G = 1$);
- Rank reduction of the Slater-type basis ($R_G = O(\log \varepsilon^{-1})$, up to the tolerance $\varepsilon > 0$, cf. [18]);
- Using the united (agglomerated) orthogonal Tucker vectors, whose rank is supposed to be weakly dependent on the particular molecule and the grid parameters [22, 23, 24].

All these concepts still require further theoretical and numerical analysis and will be addressed alsewhere.

The main advantage of the low tensor rank approximating basis sets is the linear scaling of the resultant algorithms in n, that already allows to advent the huge $n \times n \times n$-grids in $\mathbb{R}^3$ (specifically, $n \leq 2 \cdot 10^4$, in the contemporary computing practice on the base of tensor-structured methods). This can be the important benefit in the FEM-DFT computations applied to large molecular clusters.

2.5 Tensor computation of the Galerkin integrals in $J(C)$, $K(C)$

The benefitial fieture of our method is that functions and operators involved in the computational scheme (2.8) - (2.12) are efficiently evaluated using (approximate) low-rank tensor-product representations in the basis sets $\{G_\mu\}$ and $\{X_\mu\}$ at the expence that scales linear-logarithmic in n, $O(n \log n)$.

To that end, we introduce some interpolation/prolongation operators interconnecting the continuous functions on Ω and their discrete representation on the grid via the coefficients tensors in $\mathbb{R}^{\mathcal{I}}$ (or in $\mathbb{R}^{\mathcal{J}}$). Note that the coefficients space of 3-tensors

$$\mathbb{V}_n = \mathbb{R}^{\mathcal{I}} := V_1 \otimes V_2 \otimes V_3,$$

is the tensor-product space with $V_\ell = \mathbb{R}^n$, $(\ell = 1, 2, 3)$, cf. Appendix. Conventionally, we use the canonical isomorphism between $\mathcal{V}_n$ and $\mathbb{V}_n$,

$$\mathcal{V}_n \ni f(x) = \sum_{\mathbf{i}} f_{\mathbf{i}} \phi_{\mathbf{i}}(x) \quad \Longleftrightarrow \quad F := [f_{\mathbf{i}}]_{\mathbf{i}\in\mathcal{I}} \in \mathbb{V}_n.$$

We make use of similar entities for the pair $\mathcal{W}_n$ and $\mathbb{W}_n = \mathbb{R}^{\mathcal{J}} := W_1 \otimes W_2 \otimes W_3$, with $W_\ell = \mathbb{R}^{n-1}$, $(\ell = 1, 2, 3)$.

Now we define the collocation and L^2-projection mappings onto $\mathbb{V}_n$. For the continuous function f, we introduce the collocation "projection" operator by

$$\mathcal{P}_C : f \mapsto \sum_{\mathbf{i}} f_(y_{\mathbf{i}}) \phi_{\mathbf{i}}(x) \quad \Longleftrightarrow \quad F := [f(y_{\mathbf{i}})]_{\mathbf{i}\in\mathcal{I}} \in \mathbb{V}_n,$$

where $\{y_{\mathbf{i}}\}$ is the set of cell-centered points with respect to the grid $\omega_{\mathbf{3},n}$. Furthermore, for functions $f \in L^2(\Omega)$, we define L^2-projection by

$$\mathcal{P}_0 : f \mapsto \sum_{\mathbf{i}} \langle f, \phi_{\mathbf{i}} \rangle \phi_{\mathbf{i}}(x) \quad \Longleftrightarrow \quad F := [\langle f, \phi_{\mathbf{i}} \rangle]_{\mathbf{i}\in\mathcal{I}} \in \mathbb{V}_n.$$

Likewise, we denote the L^2-projection onto $\mathbb{W}_n$ by $\mathcal{Q}_0$.

Using the discrete representations as above, we are able to rewrite all functional and integral transforms in (2.8) - (2.12), in terms of tensor operations in $\mathbb{V}_n$. In particular, for the continuous targets, the function-times-function, and the L^2-scalar product can be dicretised by tensor operations as

$$f \cdot g \mapsto F \odot G \in \mathbb{V}_n, \quad \text{and} \quad \langle f, g \rangle \mapsto h^3 \langle F, G \rangle,$$

with

$$F = \mathcal{P}_C(f), \quad G = \mathcal{P}_C(g),$$

where the scaling constant defines the grid-cell volume h^3, and $\odot$ means the Hadamard (entrywise) product of tensors.

The convolution product is represented by

$$f * g \mapsto F *_T G \in \mathbb{V}_n, \quad \text{with} \quad F = \mathcal{P}_C(f) \in \mathbb{V}_n,\ G = \mathcal{P}_0(g) \in \mathbb{V}_n,$$

where the tensor operation $*_T$ stands for the tensor-structured convolution transform in $\mathbb{V}_n$ described in [19] (see also [24, 23] concerning the application of fast $*_T$ transform in electronic structure calculations). Related to *separable quadrature* assumption (cf. item (D) in §2.3), we notice that under certain assumptions on the regularity of the input functions the tensor product convolution $*_T$ can be proven to provide the approximation error of order $O(h^2)$, while the two-grid version via the Richardson extrapolation leads to the improved error bound $O(h^3)$ (cf. [19]).

Representations (2.8) - (2.9) can be now rewritten (approximately) in the discrete tensor form as follows,

$$\rho \approx \Theta := \sum_{a=1}^{N} \left(\sum_{\kappa,\lambda=1}^{N_b} C_{\kappa a} C_{\lambda a} G_\kappa \odot G_\lambda \right), \quad \text{where} \quad G_\kappa = \mathcal{P}_C(g_\kappa),$$

and then

$$V_H = \rho * g \approx \Theta *_T P_N, \quad \text{where} \quad P_N = \mathcal{P}_0(g),\ g = \frac{1}{\|\cdot\|}, \tag{2.15}$$

with $P_N \in \mathbb{V}_n$ being the collocation tensor for the Coloumb potential. This implies the tensor representation of the Coloumb matrix,

$$J(C)_{\mu\nu} \approx \langle G_\mu \odot G_\nu, \Theta *_T P_N \rangle, \quad 1 \le \mu, \nu \le N_b. \tag{2.16}$$

The separability property (A) ensures that $rank(G_\mu) \le R_G$, while tensors Θ and P_N are to be approximated by low-rank tensors. Hence, in our method, the corresponding tensor operations are implemented using fast multilinear algebra accomplished with the corresponding rank optimization (tensor truncation).

Likewise, tensor representations (2.10) - (2.12) realised in [17], now look as follows,

$$W_{a\nu} \approx \Upsilon_{a\nu} := \left[G_\nu \odot \sum_{m=1}^{N_b} C_{ma} \odot G_m \right] *_T P_N, \quad \nu = 1, ..., N_b, \tag{2.17}$$

with the tensor $P_N \in \mathbb{V}_n$ defined by (2.15),

$$K_{\mu\nu,a} \approx \chi_{\mu\nu,a} := \langle \left[\sum_{m=1}^{N_b} C_{ma} G_m \right] \odot G_\mu, \Upsilon_{a\nu} \rangle, \quad \mu, \nu = 1, ..., N_b, \tag{2.18}$$

finally providing the entries of the exchange matrix,

$$K(C)_{\mu\nu} = \sum_{a=1}^{N} \chi_{\mu\nu,a}, \quad \mu, \nu = 1, ..., N_b. \tag{2.19}$$

Again, the auxiliary tensors and respective algebraic operations have to implemented with truncation to low-rank tensor formats.

Notice that the core Hamiltonian $H = \{h_{\mu\nu}\}$ can be computed by the respective tensor operations in $\mathbb{W}_n$, and $\mathbb{V}_n$,

$$h_{\mu\nu} \approx \frac{1}{2} \langle \nabla_T \overline{G}_\mu, \nabla_T \overline{G}_\nu \rangle_{(\mathbb{W}_n)^3} + \langle V_0, G_\mu \odot G_\nu \rangle_{\mathbb{V}_n}, \quad 1 \le \mu, \nu \le N_b, \tag{2.20}$$

where $V_0 = \mathcal{P}_0(V_c) \in \mathbb{V}_n$, and where the rank-$R_G$ tensors $\overline{G}_\mu$ ($\mu = 1, ..., N_b$) represent the Galerkin basis functions g_μ in $\mathbb{W}_n$ by $\overline{G}_\mu = \mathcal{Q}_0(g_\mu)$. Furthermore, the operator

$$\nabla_T : \mathbb{W}_n \to (\mathbb{W}_n)^3 := \{ \mathbf{w} = \begin{pmatrix} w_1 \\ w_2 \\ w_3 \end{pmatrix} : w_k \in \mathbb{W}_n,\ k = 1, 2, 3 \},$$

denotes the discrete gradient map by 3-way central differences at $y_{\mathbf{j}}$, $\mathbf{j} \in \mathcal{J}$, where $(\mathbb{W}_n)^3$ is the "vector space" of 3-tensors.

With the particular requirements on the rank, $rank(\overline{G}_\mu) \le R_G$, the operator ∇_T applies to each individual rank-1 canonical 3-tensor in $\mathbb{W}_n$ by

$$\nabla_T (x_1 \otimes x_2 \otimes x_3) := \begin{pmatrix} \nabla_1 x_1 \otimes x_2 \otimes x_3 \\ x_1 \otimes \nabla_2 x_1 \otimes x_3 \\ x_1 \otimes x_2 \otimes \nabla_3 x_3 \end{pmatrix} \in (\mathbb{W}_n)^3,$$

where the univariate discrete gradient matrix ∇_k $(k = 1, 2, 3)$ is defined conventionally by central differences on the vectors in $\mathbb{R}^{n-1}$ with zero extension, imposed by the homogeneous Dirichlet boundary conditions (recall that $\mathcal{W}_n \in H_0^1(\Omega)$).

3 Multilevel tensor-truncated SCF iteration via DIIS

3.1 General SCF iteration

The standard SCF algorithm can be formulated as the following "fixed-point" iteration: Starting from initial guess C_0, perform iterations of the form

$$\begin{aligned} \widetilde{F}_k C_{k+1} &= S C_{k+1} \Lambda_{k+1}, \quad \Lambda_{k+1} = \mathrm{diag}(\lambda_1^{k+1}, ..., \lambda_N^{k+1}) \\ C_{k+1}^* S C_{k+1} &= I_N, \\ D_{k+1} &= C_{k+1} C_{k+1}^*, \end{aligned} \tag{3.1}$$

where $\widetilde{F}_k$, $k = 0, 1, ...$, is specified by the particular method of choice. For example, for the simplest approach, called the *Roothaan algorithm*, one has $\widetilde{F}_k = F(C_k)$. In practically interesting situations this algorithm usually leads to "flip-flop" stagnation.

Recall that here, $\lambda_1^{k+1} \le \lambda_2^{k+1} \le ... \le \lambda_N^{k+1}$ are the smallest N eigenvalues of the linear generalized eigenvalue problem

$$\widetilde{F}_k U = \lambda S U,$$

and C_{k+1} are $N_b \times N$ matrices containing the respective N orthonormal eigenvectors.

We propose a modification to the standard SCF iteration that includes its implementation on a sequence of successively refined grids with the grid-dependent stopping criteria. We use the particular choice of $\widetilde{F}_k$, $k = 0, 1, ...$, via the DIIS-algorithm, (cf. [30]), with the starting value $\widetilde{F}_0 = F(C_0) = H$. The principal feature of our tensor-truncated iteration is revealed on the fast update of the Fock matrix $F(C)$ by using tensor-product multilinear algebra of 3-tensors described in §2.5, and accomplished with the rank truncation.

3.2 SCF iteration using DIIS scheme

Recall that in the case of orthonormal basis, i.e., the overlap matrix equals identity, the DIIS iteration is substituated by the commutation property, $[F(D), D] = 0$, on the exact solution. In the general case, the DIIS algorithm is based on the fact that the equation

$$e(C) := F(C)DS - SDF(C) = 0$$

is the equivalent formulation of the initial Hartree-Fock Galerkin equation (2.7), see [26].

In the present paper, we use the original version of DIIS scheme, defined by the following choice of the *residual error vectors* (cf. [15]),

$$e(C_i) := [C_i^* F(C_i) C_i]_{|\{1 \le \mu \le N; N+1 \le \nu \le N_b\}} \in \mathbb{R}^{N \times (N_b - N)}, \quad i = 0, 1, ..., k, \tag{3.2}$$

that should wanish on the exact solutions of the Hartree-Fock Galerkin equation due to the orthogonality constraint.

The minimizing coefficients vector $\overline{c} := (c_0, ..., c_k)^T \in \mathbb{R}^{k+1}$ is being computed by solving the constrained quadratic minimisation problem for the respective cost functional (the averaged residual error vector over previous iterands),

$$f(\overline{c}) := \frac{1}{2}\left\|\sum_{i=0}^{k} c_i e(C_i)\right\|_0^2 \equiv \frac{1}{2}\langle B\overline{c}, \overline{c}\rangle \to \min, \quad \text{provided that} \quad \sum_{i=0}^{k} c_i = 1,$$

where

$$B = \{B_{ij}\}_{i,j=0}^{k} \quad \text{with} \quad B_{ij} = \langle e(C_i), e(C_j)\rangle,$$

and with $e(C_i)$ defined by (3.2). Introducing the Lagrange multiplier λ, the problem is reduced to minimization of the Lagrangian functional

$$L(\overline{c}, \lambda) = f(\overline{c}) - \lambda(\langle \mathbf{1}, \overline{c}\rangle - 1),$$

where $\mathbf{1} = (1, ..., 1)^T \in \mathbb{R}^{k+1}$, that leads to the linear augmented system of equations

$$\begin{aligned} B\overline{c} - \lambda\mathbf{1} &= 0, \\ \langle \mathbf{1}, \overline{c}\rangle &= 1. \end{aligned} \tag{3.3}$$

Finally, the Fock operator $\widetilde{F}_k$ is built up by

$$\widetilde{F}_k = \sum_{i=0}^{k-1} c_i^{opt} \widetilde{F}_i + c_k^{opt} F(C_k), \quad k = 0, 1, 2, ..., \tag{3.4}$$

where the minimizing coefficients $c_i^{opt} = \overline{c}_i$ $(i = 0, 1, ..., k)$ solve the linear system (3.3). Now check the stopping criteria and solve, if required, the eigenvalue problem (3.1) for C_{k+1}.

Note that in practice one can compute the averaged residual vector on a reduced subsequence of iterands, $e(C_k), e(C_{k-1}), ..., e(C_{k-k_0})$.

3.3 Tensor-truncated multilevel DIIS iteration

Now we describe the resultant numerical algorithm. Recall that the discrete Fock operator is specified by the matrix

$$F(C) = H + J(D) + K(D), \quad D = 2CC^* \in \mathbb{R}^{N_b \times N_b},$$

where the core Hamiltonian and the Hartree and exchange operators are given by tensor representations (2.20), (2.16) and (2.19), respectively.

First, we describe the unigrid tensor-truncated DIIS scheme.

Algorithm TT_DIIS *(Unigrid tensor-truncated DIIS scheme).*

0. *Given the grid parameter n and termination parameter $\varepsilon_n > 0$.*

1. *Compute the core Hamiltonian matrix H. Set up $J = 0$, $K = 0$, and initialize C_0 as the solution of (3.1) providing $\widetilde{F}_0(C_0) = H$.*

For $k = 0, 1, ...,$ perform

2a. *Solve the full linear eigenvalue problem of size $N_b \times N_b$,*

$$\widetilde{F}_k U = \lambda S U,$$

and define C_{k+1} as matrices containing the respective N orthonormal eigenvectors.
2b. *Compute $F(C_{k+1})$ in tensor format via discrete representations in $\mathbb{V}_n$ and $\mathbb{W}_n$ described in §2.5, and update $\widetilde{F}_{k+1}$ by DISS scheme (3.4).*
2c. *Terminate iteration by checking the stoping criteria $\|e(C_{k+1}) - e(C_k)\| \le \varepsilon_n$.*

The multilevel version of Algorithm **TT_DIIS** is defined on a sequence of grid parameters $n_p = n_0, 2n_0, \ldots, 2^M n_0$, $p = 0, ..., M$, corresponding to the succession of dyadically refined spacial grids. Denote the computed spectral data at level p by $\lambda_p^* \in \mathbb{R}^N$ and $C_p^* \in \mathbb{R}^{N_b \times N}$, and let $k_p = 1, ...$ be the number of DIIS iterations at level p.

Algorithm MTT_DIIS *(Multilevel tensor-truncated DIIS scheme).*
0. *Given the coarse grid parameter n_0, termination parameter $\varepsilon_0 > 0$, and the number of grid refinements M.*
1. *For $p = 0$ apply Algorithm* **TT_DIIS** *with $n = n_0$, $\varepsilon_n := \varepsilon_0$.*
2. *For $p = 1, ..., M$ apply Algorithm* **TT_DIIS** *successively with the input parameters $n_p := 2^p n_0$, $\varepsilon_p := \varepsilon_0 2^{-2p}$, and $\widetilde{F}_{k-1}$, keeping the continuous numbering of the DIIS iterations starting from, $k = 1 + \sum_{\ell=0}^{p-1} k_\ell$. Count the curent number of iterations on level p, k_p.*
3. *Compute final solution pair by the Richardson extrapolation of data corresponding to the grid parameters n_M and n_{M-1},*

$$\widetilde{\lambda} = (4\lambda_M^* - \lambda_{M-1}^*)/3, \quad \widetilde{C} = (4C_M^* - C_{M-1}^*)/3.$$

In large scale computations to be presented in §4, the multilevel Algorithm **MTT_DIIS** allows us to perform most of iterative steps on coarse grids thus reducing dramatically the computational cost, and at the same time, providing the good initial guess for DIIS iteration on nonlinearity at each approximation level.

3.4 Complexity estimate in terms of R_G, N_b and n

The rest of this section addresses the complexity estimate of the multilevel tensor-truncated iteration in terms of R_G, N_b, n and other governing parameters of the algorithm.

Lemma 3.1 *Let $rank(G_\mu) \le R_G$ and $rank(P_N) \le R_N$. Suppose that canonical rank reduction of convolution products $\Upsilon_{a\nu}$ in (2.17) provides the estimate $rank(\Upsilon_{a\nu}) \le r_0$. Then the numerical cost of one iterative step in Algorithm* **MTT_DIIS** *at level p, can be bounded by*

$$Q = O(N_b R_G^2 R_N n_p \log n_p + N_b^3 R_G^2 r_0 R_N n_p).$$

Assume that the number of multigrid DIIS iterations at each level is bounded by the unique constant I_0, then the total cost of Algorithm **MTT_DIIS** *does not exceed the double cost at the finest level $n = n_M$, $2Q = O(I_0 N_b^3 R_G^2 r_0 R_N n)$.*

Proof. The rank bound $rank(g_k) \le R_G$ implies $rank(\sum_{m=1}^{N_b} C_{ma} \odot G_m) \le R_G N_b$. Hence, the numerical cost to compute tensor-product convolution $\Upsilon_{a\nu}$ in (2.17) amounts to

$$Q(\Upsilon_{a\nu}) = O(N_b R_G^2 R_N n_p \log n_p).$$

Since the initial canonical rank of $\Upsilon_{a\nu}$ is estimated by $rank(\Upsilon_{a\nu}) \le N_b R_G^2 R_N$, the multigrid rank reduction algorithm, having linear scaling in $rank(\Upsilon_{a\nu})$ (cf. [23]), provides the complexity bound $O(r_0 N_b R_G^2 R_N n_p)$. Hence the total cost to compute scalar products in $\chi_{\mu\nu,a}$ (see (2.18)) can be estimated by

$$Q(\chi_{\mu\nu,a}) = O(N_b^3 R_G^2 r_0 R_N n_p),$$

which completes the first part of our proof. The second assertion is due to the linear scaling of unigrid algorithm in n_p, so that we arrive at the bound

$$n_0 + 2n_0 + ... + 2^p n_0 \le 2^{p+1} n_0 = 2n_M,$$

that proves our claim. ■

Remark 3.2 *Notice that in the case of large molecules further optimisation of the algorithm up to $O(R_N N_b^2 n_p)$-complexity is possible on the base of rank reduction applied to the rank-$R_G N_b$ orbitals and by using an iterative eigenvalue solver instead of currently employed direct solver by diagonalization.*

4 Numerical illustrations

4.1 General discussion

Our algorithm for the *ab initio* solution of the Hartree-Fock equation in *tensor-structured format* is examined numerically on some moderate size molecules. These include the all electron case of H_2O, and the case of pseudopotential of CH_4 and CH_3OH molecules. In the present numerical examples, we use the discrete GTO basis functions for the reasons of convenient comparison of the results with the output from the standard MOLPRO package based on the analytical evaluation of the integral operators in the GTO basis.

The size of the computational box introduced in §2.3 varies from $2b = 11.21$ $\mathring{A}$ and $2b = 15.45$ $\mathring{A}$ for H_2O, and CH_4 molecules, respectively. The finest step-size of the grid $h = 0.0027$ $\mathring{A}$ is reached in the SCF iterations for H_2O molecule, using the finest level grid with $n = 4096$, while the average step size for the computations using the pseudopotentials of the moderate size molecules is about $h = 0.015$ $\mathring{A}$, corresponding to the grid size $n = 1024$.

Using the equidistant $n \times n \times n$ tensor grid given by (2.13), the functions in $\mathcal{V}_n$ of the type (2.14) are discretized in the intervals $[-b, b]$, with b depending on the molecule size. In this way, we obtain the canonical representation of the electron densities and orbitals on 3D Cartesian grid, further applied for the tensor-structured calculation of the Hartree (2.2) and the nonlocal exchange (2.3) potentials. Notice, that the Galerkin representation of the exchange operator leads to the evaluation of the six-dimensional integral over $\mathbb{R}^3 \times \mathbb{R}^3$, which formerly stated complicated problems for its analytical computation. Our tensor-structured techniques provide means for the discrete evaluation of this integral using the fast tensor-product convolution and other tensor-product operations which are of linear complexity with respect to the one-dimension grid size n. The convolving Poisson kernel is effectively represented in the rank-R_N canonical format with the rank parameter in the range $20 \le R_N \le 30$, depending logarithmically on the univariate grid size n, $R_N = O(\log n)$.

4.2 Tensor computation of the Coulomb and exchange matrices

A detailed description of the tensor-product numerical schemes for the Coulomb and exchange matrices in the case of closed shell systems is presented in [23, 17]. In this section, we verify the performance of the tensor-structured computations of the Coulomb and exchange matrices by using the *true solutions for the orbitals* of molecules, taking the expansion coefficients $C_{\mu i}$ for the GTO basis in (2.4) from the MOLPRO package.

The orbitals and the electron density are discretized in the corresponding computational box, thus yielding the canonical representation of the relevant functions (electron density and orbitals) on 3D Cartesian grid. The Hartree and exchange potentials and their Galerkin representations in the GTO basis, are then computed numerically using the tensor-product operations for the canonical and Tucker tensors (see Appendix), which exhibit the linear complexity with respect to one-dimension grid size n.

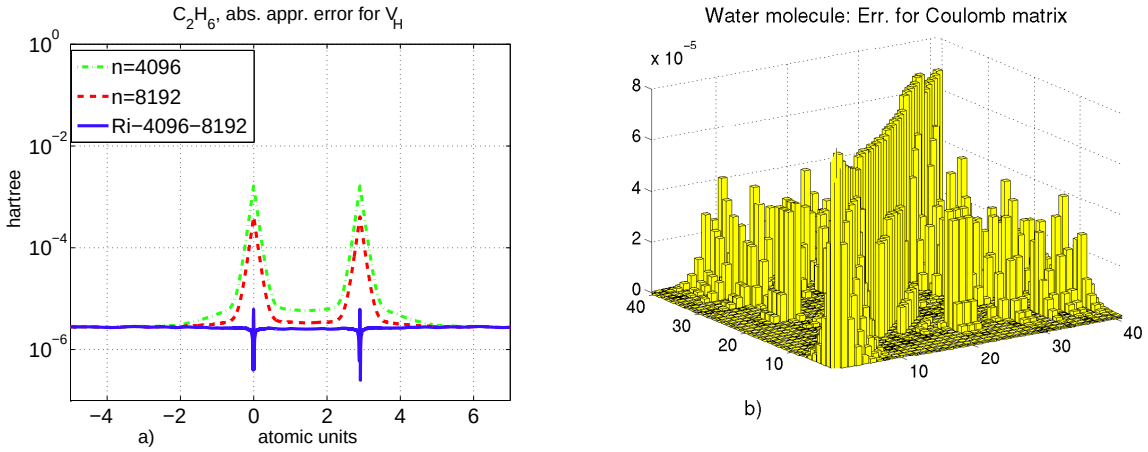

Figure 4.1: Left: Absolute approximation error (blue line: $\approx 10^{-6}$) in the tensor-product computation of the Hartree potential of C_2H_6, measured in the grid line $\Omega = [-5, 7] \times \{0\} \times \{0\}$. Right: the absolute error for the Coulomb matrix of H_2O, ($\approx 10^{-5}$).

The Coulomb (Galerkin) matrix of the Hartree potential, V_H, is computed by tensor inner products in $\{g_k\}$,

$$J_{km} := \int_{\mathbb{R}^3} g_k(x) V_H(x) g_m(x) dx, \quad k, m = 1, \dots R_0, \quad x \in \mathbb{R}^3.$$

Figure 4.1,left shows the absolute approximation error (blue line: $\approx 10^{-6}$) in the tensor-product representation of the Hartree potential of C_2H_6 molecule, measured in the subinterval $\Omega = [-5, 7] \times \{0\} \times \{0\}$. Figure 4.1,right presents the absolute accuracy for the Coloumb matrix of H_2O, computed by tensor-structured techniques on the large grid with the one-dimension size $n = 8192$, providing the absolute accuracy $\approx 10^{-5}$. This corresponds to the approximation error $O(h^3)$ achieved on the grid with high resolution, $h \approx 0.0008$ $\mathring{A}$.

The exchange matrix in the Galerkin GTO basis is given by

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

Figure 4.2,right shows the L^∞-error in the matrix elements of K for the pseudodensity of CH_3OH computed on the grid with $n = 1024$. Figures 4.2,left illustrate high accuracy achieved in the computation of the exchange matrix of H_2O molecule on the grids $n = 8192$, that corresponds to the fine step-size $h \approx 0.0016$ $\overset{\circ}{A}$, and the asymptotic approximation error $O(h^3)$, $h = 1/n$.

4.3 Multilevel tensor-truncated SCF iteration

The tensor-structured algorithms for the calculation of the Coulomb and exchange parts of the Fock operator pioneer the way to solve numerically the *ab initio* Hartree-Fock equation, by using Algorithms **TT_DIIS** and **MTT_DIIS** in §3.3. Starting with the zero initial guess for matrices $J(D) = 0$ and $K(D) = 0$ in the Galerkin Fock matrix (2.6), we solve the eigenvalue problem at the first iterative step ($p = 0$) using only the H part of the Fock matrix in (2.6), that does not depend on the solution.

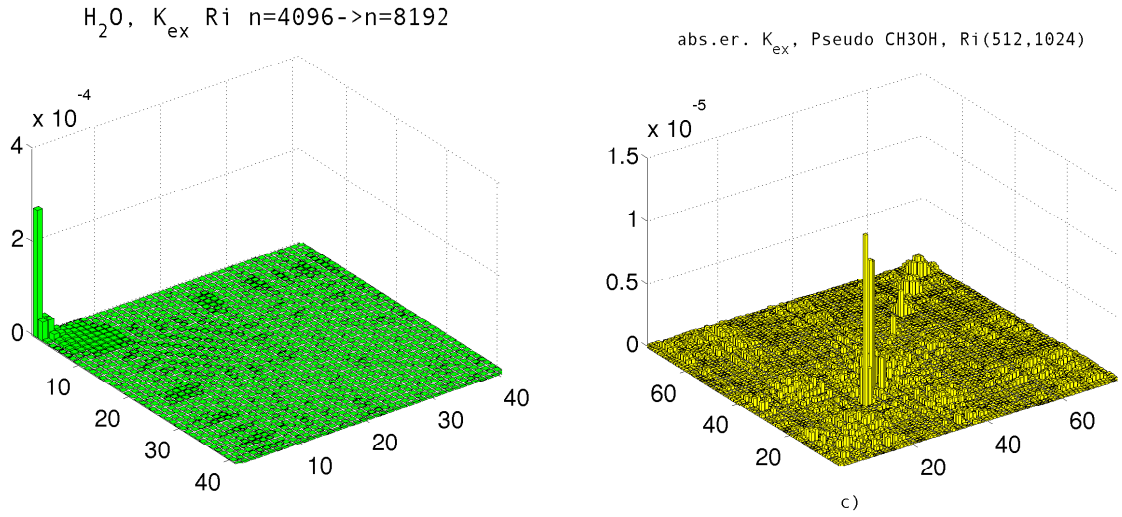

Figure 4.2: L^∞-error in $K_{ex} = K$ for the density of H_2 and pseudodensity of CH_3OH.

Thus, SCF iterations start with the expansion coefficients $C_{\mu i}$ for orbitals in the GTO basis, computed using only the core Hamiltonian $\mathcal{H}$. At every iteration step, the Hartree and exchange potentials and the corresponding Galerkin matrices, are computed using the updated expansions coefficients $C_{\mu i}$. The renewed Coloumb and exchange matrices are again used in the updated Fock matrix for the solution of the eigenvalue problem. The L^∞-error in the virtual block of the Fock operator in solutions of the consequent iterations, $e(C_k)$, is used as the residual for the convergence control. Figure 4.3 shows the convergence of the single-grid scheme for the solution of the Hartree-Fock equation in the pseudopotential case of CH_4.

The multilevel solution of the nonlinear eigenvalue problem (2.7) is realised via SCF iteration on a sequence of uniform grids, beginning from the initial coarse grid, say, with $n_0 = 64$, and proceeding on the diadically refined grids, $n_p = n_0 2^p$, $p = 1, ..., M$. We use the grid dependent termination criteria $\varepsilon_{n_p} := \varepsilon_0 2^{-2p}$, keeping the continuous numbering of the iterations. Figure 4.4 (left) shows the convergence of the iterative scheme in the case of

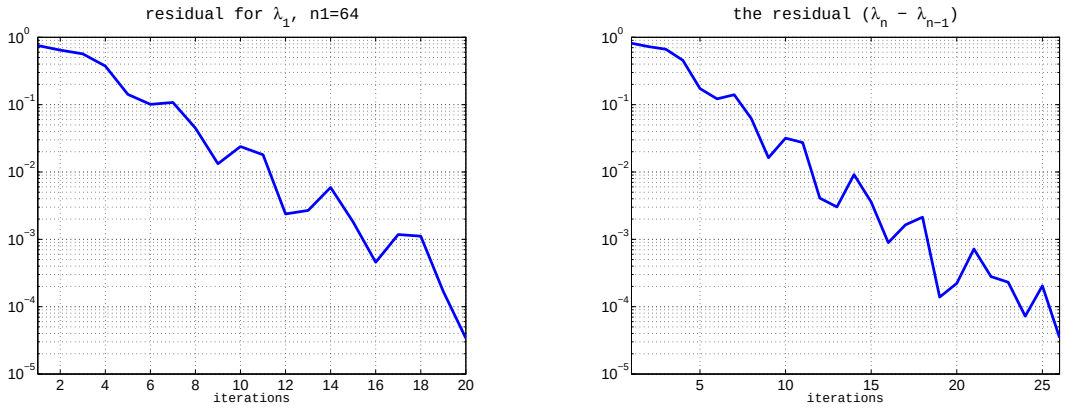

Figure 4.3: Convergence of the unigrid SCF iteration for the pseudopotentail case of the CH_4 molecule on the grid sizes $n = 64$ (left) and $n = 256$ (right).

pseudopotential of CH_4. Convergence in the total Hartree-Fock energy reaching the absolute error $9 \cdot 10^{-6}$ on the grid size $n = 1024$ is shown in Figure 4.4 (right). The total energy is calculated by

$$E_{HF} = 2\sum_{a=1}^{N} \lambda_a - \sum_{a=1}^{N} \left(\widetilde{J}_a - \widetilde{K}_a \right)$$

with $\widetilde{J}_a = (\psi_a, V_H \psi_a)_{L^2}$, and $\widetilde{K}_a = (\psi_a, \mathcal{V}_{ex} \psi_a)_{L^2}$, being the so-called Coulomb and exchange integrals, respectively, computed in the orbital basis ψ_a $(a = 1, ..., N)$.

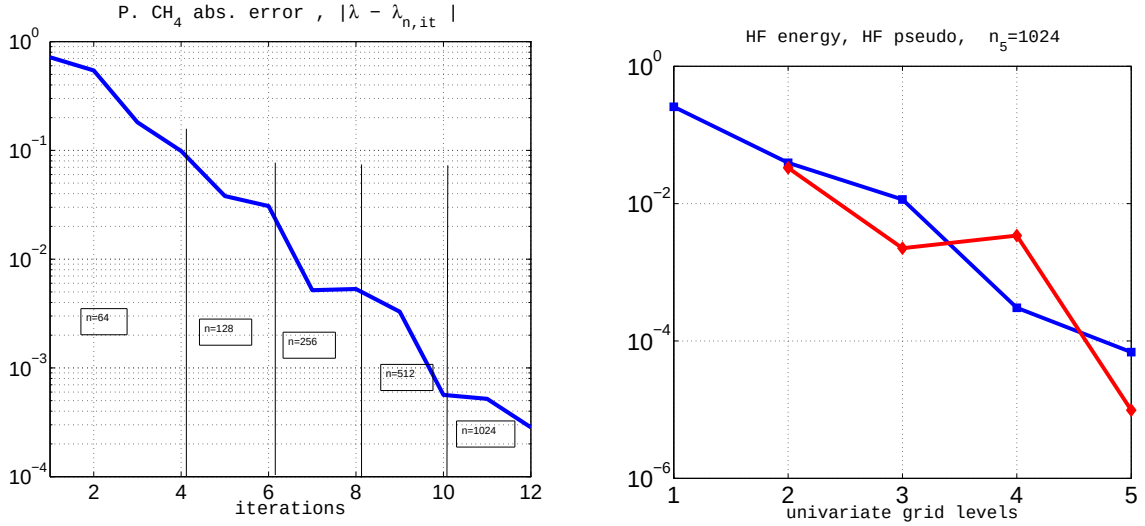

Figure 4.4: Multilevel convergence (left) for the pseudopotential of CH_4 molecule, and convergence of the HF energy in the grid levels (right). The initial level 1 corresponds to $n = 64$, while the final level 5 corresponds to $n = 1024$.

Figure 4.5 (left) shows the linear scaling in n, corresponding to CPU time at one iteration.

Figure 4.5 (right) shows the number of "effective" iterations counted by rescaling the total computational time to the iteration time-unit observed at each iterative step at the finest grid-level.

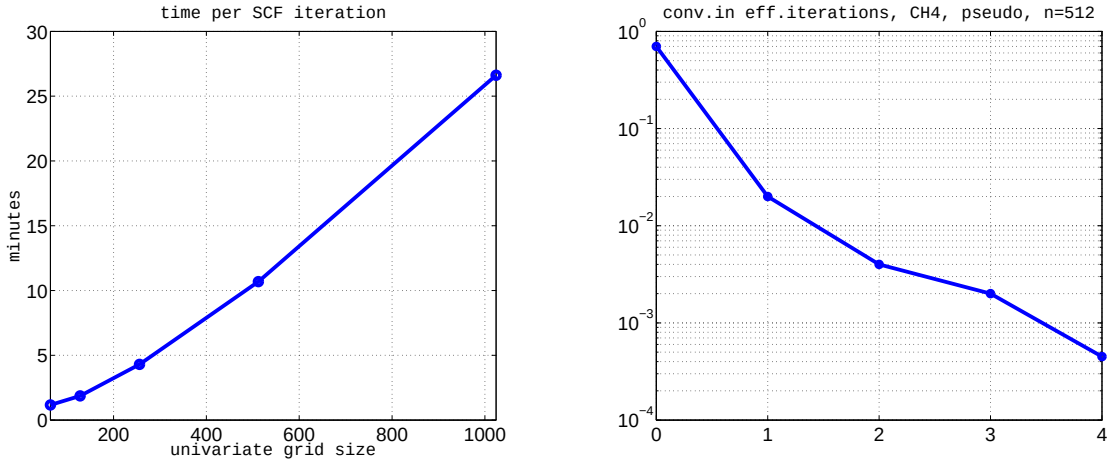

Figure 4.5: Linear scaling in n (left) and convergence in the effective iterations (right).

Figure 4.6 represents the convergence history of the nonlinear iteration for CH_3OH measured by the iteration residual error (left), and by the energy error (right), respectively.

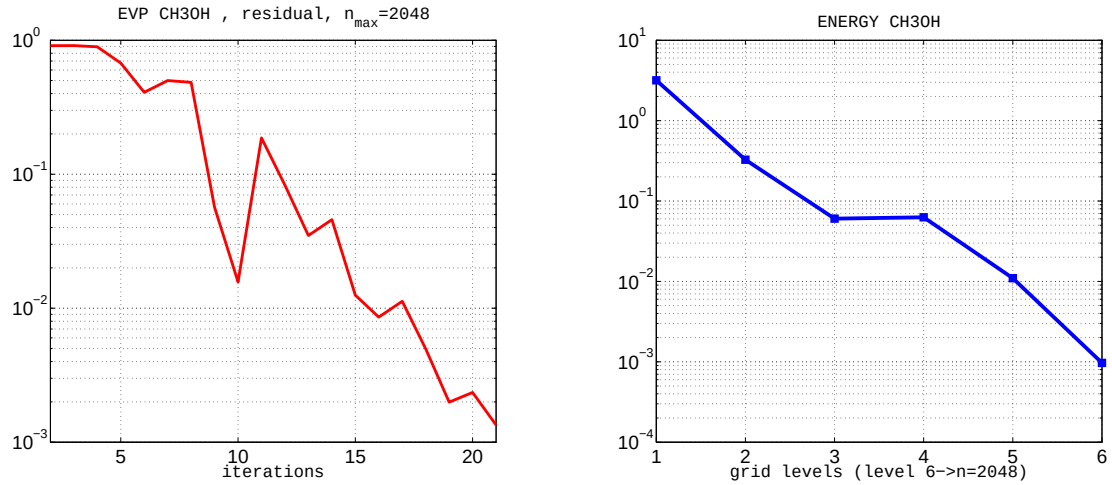

Figure 4.6: Residual (left) and the energy (right) iteration history for CH_3OH molecule.

Figure 4.7 (left) shows convergence of the SCF iteration for all electron case of H_2O. This challenging problem is solved efficiently due to usage of large 3D Cartesian grids up to the volume size $N = 8192^3$. Figure 4.7 (right) shows convergence of the HF energy for the corresponding grid levels.

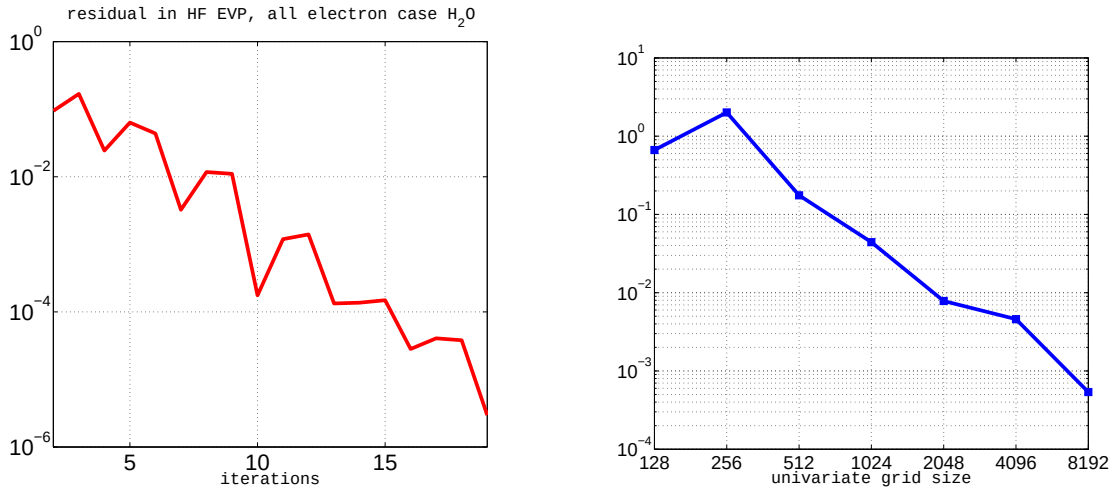

Figure 4.7: Multilevel convergence of the SCF iteration applied to the all electron case of H_2O (left), and convergence in the energy in n (right).

5 Conclusions and further perspectives

We present the grid-based tensor-truncated numerical method for the robust and accurate iterative solution of the self-consistent Hartree-Fock equation at the cost $O(N^{1/3})$ in the volume size $N = n^3$, over the 3D Cartesian grid. The computational scheme is based on the discrete tensor representation of the Fock operator at each step of the multilevel SCF iteration applied to the nonlinear 3D eigenvalue problem.

This scheme is neither restricted to the analytically separable basis functions like GTO orbitals nor to the traditional plane waves approximations. The Galerkin basis can be modified by adapting to the particular problem in the framework of the tensor-structured solution process.

Further improvement of the algorithm toward the $O(\log n)$-complexity on the base of quantics approximation [20], may open new perspectives for efficient *ab initio* numerical simulation of complex molecules and for the FEM-DFT computations of large molecular clusters.

The main computational blocks of the numerical scheme allow the natural parallelization on the level of matrix elements computation, rank decompositions, and the multilinear tensor operations.

6 Appendix: Description of tensor-structured formats

Let $\mathbb{H} = H_1 \otimes ... \otimes H_d$ be a tensor-product Hilbert space (see [31]), where H_ℓ ($\ell = 1, ..., d$) is a real, separable Hilbert space of functions of the continuous or discrete argument (say, $H_\ell = L^2([a, b])$ or $H_\ell = \mathbb{R}^n$). Each $w \in \mathbb{H}$ can be written as a sum of rank-1 (elementary, separable) tensors

$$w = \sum_k w_k^{(1)} \otimes w_k^{(2)} \otimes \ldots \otimes w_k^{(d)} \quad (w_k^{(\ell)} \in H_\ell).$$

The scalar product of rank-1 tensors in $\mathbb{H}$ is defined by

$$\langle w^{(1)} \otimes \ldots \otimes w^{(d)}, h^{(1)} \otimes \ldots \otimes h^{(d)} \rangle = \prod_{\ell=1}^{d} \langle w^{(\ell)}, h^{(\ell)} \rangle.$$

A dth order tensor is a function of d discrete arguments, $f : \mathbb{R}^{I_1 \times \ldots \times I_d} \to \mathbb{R}$, specified by a multi-dimensional array over $\mathcal{I} = I_1 \times ... \times I_d$, with $I_\ell = \{1, ..., n_\ell\}$, $\ell = 1, ..., d$. We write

$$V = [v_{i_1,\ldots,i_d} : i_\ell \in I_\ell] \in \mathbb{R}^{\mathcal{I}}, \quad \ell = 1, ..., d,$$

to denote a real-valued dth order tensor, that is an element of the tensor-product Hilbert space $\mathbb{H} := \mathbb{V}_{\mathbf{n}} = \otimes_{\ell=1}^{d} \mathbb{V}_\ell$, with $\mathbb{V}_\ell = \mathbb{R}^{I_\ell}$, and $\mathbf{n}$ being the d-tuple $(n_1, ..., n_d)$. $\mathbb{V}_{\mathbf{n}}$ is equipped with the Euclidean *inner product* $\langle \cdot, \cdot \rangle : \mathbb{V}_{\mathbf{n}} \times \mathbb{V}_{\mathbf{n}} \to \mathbb{R}$. Tensor $V \in \mathbb{V}_{\mathbf{n}}$ requires $\prod_{\ell=1}^{d} n_\ell$ reals for storage.

The concept of tensor methods is based on approximation of multivariate functions with low separation rank. In particular, we are interested in decomposition of a tensor $f \in \mathbb{V}_{\mathbf{n}}$, in the set of separable tensors, i.e., in some classes $\mathcal{S} \subset \mathbb{V}_{\mathbf{n}}$ of "rank structured" elements based on sums of rank-1 tensors. In this way, the canonical rank-1 tensor is represented by *outer product* of vectors $t^{(\ell)} = \{t^{(\ell)}_{i_\ell}\}_{i_\ell \in I_\ell} \in \mathbb{V}_\ell$ ($\ell = 1, ..., d$),

$$T \equiv [t_{\mathbf{i}}]_{\mathbf{i} \in \mathcal{I}} = t^{(1)} \otimes ... \otimes t^{(d)} \in \mathbb{V}_{\mathbf{n}} \quad \text{with entries} \quad t_{\mathbf{i}} = t^{(1)}_{i_1} \cdots t^{(d)}_{i_d},$$

requiring only $\sum_{\ell=1}^{d} n_\ell \ll \prod_{\ell=1}^{d} n_\ell$ reals to store it (now linear scaling in the dimension d).

In the present paper, we apply data sparse representation to high order tensors based on the Tucker and canonical models.

The rank-$(r_1, \ldots, r_d)$ *Tucker approximation* [4] is based on subspaces $\mathbb{T}_{\mathbf{n}} := \otimes_{\ell=1}^{d} \mathbb{T}_\ell$ of $\mathbb{V}_{\mathbf{n}}$ for certain $\mathbb{T}_\ell \subset \mathbb{V}_\ell$ with $r_\ell := \dim \mathbb{T}_\ell \ll n_\ell$. Given the rank parameter $\mathbf{r} = (r_1, ..., r_d)$, we denote by $\boldsymbol{\mathcal{T}}_{\mathbf{r},\mathbf{n}}$ (or simply $\boldsymbol{\mathcal{T}}_{\mathbf{r}}$) the subset of tensors in $\mathbb{V}_{\mathbf{n}}$ represented in the so-called Tucker format

$$V_{(\mathbf{r})} = \sum\nolimits_{\nu_1=1}^{r_1} \cdots \sum\nolimits_{\nu_d=1}^{r_d} \beta_{\nu_1,\ldots,\nu_d} \, t^{(1)}_{\nu_1} \otimes \ldots \otimes t^{(d)}_{\nu_d}, \tag{6.1}$$

with some vectors $t^{(\ell)}_{\nu_\ell} \in \mathbb{V}_\ell = \mathbb{R}^{I_\ell}$ ($1 \le \nu_\ell \le r_\ell$), which form the orthonormal basis of $\mathbb{T}_\ell = \mathrm{span}\{t^{(\ell)}_\nu\}_{\nu=1}^{r_\ell}$ ($\ell = 1, ..., d$). The coefficients tensor $\boldsymbol{\beta} = [\beta_{\nu_1,\ldots,\nu_d}]$, that is an element of a dual tensor space $\mathbb{V}_{\mathbf{r}} = \mathbb{R}^{r_1 \times \ldots \times r_d}$, is called the *core tensor*. The parameter $r = \max\limits_{\ell}\{r_\ell\}$ is called the maximal Tucker rank. In our applications, we normally have $r \ll n = \max n_\ell$, say $r = O(\log n)$.

Given a rank parameter $R \in \mathbb{N}$, we denote by $\boldsymbol{\mathcal{C}}_{R,\mathbf{n}} = \boldsymbol{\mathcal{C}}_R \subset \mathbb{V}_{\mathbf{n}}$ a set of tensors which can be represented in *the canonical format*

$$V_{(R)} = \sum\nolimits_{\nu=1}^{R} \mu_\nu u^{(1)}_\nu \otimes \ldots \otimes u^{(d)}_\nu, \quad \mu_\nu \in \mathbb{R}, \tag{6.2}$$

with normalized vectors $u^{(\ell)}_\nu \in \mathbb{V}_\ell$ ($\ell = 1, ..., d$). The minimal parameter R in (6.2) is called the rank (or canonical rank) of a tensor $V_{(R)}$.

The storage requirement for the Tucker (resp. canonical) decomposition is bounded by $r^d + drn$ (resp. $R + dRn$), where usually $r \ll R$.

The above defined classes of rank-structured tensors are being applied in our tensor-product approximation schemes.

It is worth to note that linear transforms of elements in tensor-structured representation are reduced to 1D-operations, that can be acomplished with the rank truncation. In particular, for tensors A_1, A_2 in the canonical format

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

we make use of the following operations:

1. Euclidean inner product (complexity $O(dR_1R_2n) \ll n^d$),

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

2. Hadamard product (complexity $O(dR_1R_2n) \ll n^d$),

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

3. Convolution of two $3rd$ order tensors A_1, A_2 (same for high order tensors),

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

with linear scaling in n, $O(R_1R_2n \log n) \ll n^3 \log n$ (corresponds to 3D FFT).

These basic properties lead to the linear scaling in n of tensor-structured multilinear algebra applied in the framework of tensor-truncated iteration.

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