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Møller-Plesset (MP2) Energy Correction Using
Tensor Factorizations of the Grid-based
Two-electron Integrals

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Møller-Plesset (MP2) Energy Correction Using Grid-based Tensor Factorization of the Two-electron Integrals

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Abstract

We present a tensor-structured method to calculate the Møller-Plesset (MP2) correction to the Hartree-Fock energy with reduced computational consumptions. The approach originates from the 3D grid-based low-rank factorization of the two-electron integrals performed by the purely algebraic optimization. The computational scheme benefits from fast multilinear algebra implemented on the separable representations of the molecular orbital transformed two-electron integrals, the doubles amplitude tensors and other fourth order data-arrays involved. The separation rank estimates are discussed. The so-called quantized approximation of the long skeleton vectors comprising the tensor factorizations of the main entities allows to reduce the storage costs. The detailed description of tensor algorithms for evaluation of the MP2 energy correction is presented. The efficiency of these algorithms is illustrated in the framework of Hartree-Fock calculations for compact molecules, including alanine and glycine amino acids.

Key words: Møller-Plesset perturbation theory, Hartree-Fock equation, two-electron integrals, truncated Cholesky factorization, tensor decompositions, quantized tensor approximation, truncated singular value decomposition.

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

1 Introduction

The Møller-Plesset perturbation theory (MP2) provides an efficient tool for a correction to the Hartree-Fock energy by relatively modest numerical efforts [1, 2, 3]. It offers the facilities for the accurate calculations of the molecular gradient energy and other quantities [4, 5]. Since the straightforward calculation of the MP2 correction scales as $O(N_b^5)$ flops with respect to the number of basis functions, efficient methods are consistently developed making the problem tractable for larger molecular systems. The direct method for evaluating the MP2 energy contribution and the energy gradient which reduces the storage needs to

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$O(N_b^2)$, at the expense of calculation time, have been introduced in [6]. The advantageous technique using the Cholesky factorization of the two-electron integrals introduced in [7] was efficiently applied for MP2 calculations [8]. A linear scaling MP2 scheme for extended systems is considered in [9]. Recently, the MP2 scheme attracted a numerous interest due to efficient algorithms for the multi-electron integrals [10, 11], the density fitting approach exhibiting a low cost when considering extended molecular systems [12, 13, 14], and owing to application of tensor factorization methods [15]. An efficient MP2 algorithm applicable for large extended molecular systems in the framework of the DFT model is based on the Laplace transform reformulation of the problem and usage of the multipole expansion [16].

Traditional approaches for the numerical solution of the Hartree-Fock equation are based on the *analytical* calculation of the arising convolution type integrals in \mathbb{R}^3 , the so-called two-electron integrals (TEI), using the naturally separable Gaussian-type basis functions. Earlier attempts towards the grid-based Hartree-Fock calculations were shown to be tractable on the examples of diatomic or “linear“ molecules, [17, 18], while the multi-resolution techniques was confined to the case of rather small compounds [19].

The tensor-structured paradigm leads to the “black-box” numerical treatment of the Hartree-Fock problem based on the representation of the basis functions in a volume box, using the $n \times n \times n$ 3D Cartesian grid positioned arbitrarily with respect to the atomic centers [20, 21]. The core Hamiltonian and the multidimensional integrals in TEI tensor, including the 3D convolution with the Newton kernel, are evaluated numerically on the grid, by the rank-structured operations in 1D complexity [22, 23, 24, 25]. Due to elimination of the analytical integrability requirements, this approach gives a choice to use rather general physically relevant basis sets represented on the grid.

The tensor-structured calculation of the 3D integral transforms is not expensive since the cubic scaling n^3 of computation complexity is *avoided* due to algebraically separable representation of variables: both storage and time scale linearly in 1D size. Though calculations are performed on the data represented in the volume with the mesh size resolution corresponding to n^3 grid points. It becomes possible due to the optimized low rank representations of the 3D functions and operators, up to the chosen tolerance $\varepsilon > 0$, controlled by the singular value decomposition (SVD) at all steps of calculations¹. High accuracy is achieved due to large grid-sizes of the order of $n \simeq 10^5$ in each variable, reproducing the approximation quality over the tensor-grid of $n^3 \simeq 10^{15}$ entries. Fine mesh resolution of the order of $h \simeq 10^{-4} \text{ \AA}$ is provided for volume box with the equal size of 40 a.u. ($\simeq 20 \text{ \AA}$) in each spatial variable.

In this paper, we present an approach for computation of the Møller-Plesset correction to the Hartree-Fock energy with reduced numerical cost, using the factorized tensor representation of TEI matrix introduced recently in [25]. Notice that the auxiliary redundancy-free factorization of TEI is obtained in a “black-box” way, without physical insight into the molecular configuration: Given the coordinates of nuclei on a fine 3D tensor grid, and the respective discretized basis functions, the TEI integrals are computed in a “blind“ way, by entirely algebraic “1D directional density fitting” approximation upon the prescribed precision. The TEI matrix is precomputed in a form of truncated Cholesky factorization inducing

¹The tensor numerical methods circumvent the redundancy of computer representation of the multidimensional functions and operators. A brief description of the tensor formats and operations is given in Appendix A.

separability in the molecular orbitals transformed TEI matrix and in the doubles amplitude tensor. This reduces the asymptotic complexity of the MP2 calculations from $O(N_b^5)$ to $O(N_b^3 N_{orb})$, where N_b is the total number of basis functions, while N_{orb} denotes the number of occupied orbitals. The rank parameter estimates for both the orbital basis transformed TEI and for the doubles amplitude tensors are presented. Furthermore, using the quantized tensor approximation (see Appendix A and [28]) of long N_b^2 -vectors in the Cholesky factor, allows to reduce systematically the storage consumption and CPU times by a factor of $\simeq 10$ in both TEI and MP2 calculations.

The efficiency of MP2 energy correction algorithm was tested for some compact molecules, including glycine and alanine amino acids. Due to factorized tensor representations of the involved multidimensional data arrays, the MP2 calculation times turned out to be quite moderate, compared with those for TEI tensor, ranging from one second for water molecule to approximately 4 minutes for glycine molecule². The numerical accuracy is controlled by the given threshold $\varepsilon > 0$, due to stable tensor-rank reduction algorithms.

The rest of the paper is organized as follows. In §2 we recall the redundancy-free representation of the TEI matrix [25] and analyze the numerical ranks of the directional “1D density fitting”. We present an algorithm which have been implemented in Matlab for the efficient truncated Cholesky decomposition of TEI matrix based on its the precomputed factorization. §3 presents the algorithm for calculation of the MP2 energy correction using the factorized tensor representation of the involved multivariate data arrays. The QTT compression ranks of long vectors comprising various tensor quantities are analyzed numerically, leading to the corresponding complexity estimates. We present numerical results for several compact molecules. Appendix A recalls the main tensor formats applied in the paper and discusses some algebraic operations on rank-structured data [21, 28]. Appendix B describes the important tensor factorization algorithms for TEI matrix implemented in Matlab and illustrates the numerical effects of quantized tensor approximation.

2 Truncated Cholesky factorization of the TEI matrix

In this section we outline the efficient algorithm for low-rank Cholesky decomposition of the TEI matrix that requires only partial information on the TEI tensor [25]. The precomputed Cholesky factorization of the TEI matrix will be the main ingredient in the tensor-based MP2 calculations.

For a finite basis set $\{g_\mu\}_{1 \leq \mu \leq N_b}$, the associated fourth order two-electron integrals (TEI) tensor, $\mathbf{B} = [b_{\mu\nu\lambda\sigma}]$, is defined entrywise by

$$b_{\mu\nu\lambda\sigma} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{g_\mu(x)g_\nu(x)g_\lambda(y)g_\sigma(y)}{\|x - y\|} dx dy, \quad \mu, \nu, \lambda, \sigma = 1, \dots, N_b. \quad (2.1)$$

The associated TEI matrix $B = [b_{\mu\nu;\lambda\sigma}]$ of size $N_b^2 \times N_b^2$, obtained by reshaping of the 4-th order tensor \mathbf{B} to a matrix over the long indices $[\mu\nu]$ and $[\lambda\sigma]$, is known to be symmetric and positive definite.

²All tensor-structured calculations are done in MATLAB using either IBM laptop, or the terminal of 8 AMD Opteron Dual-Core clusters. Implementation in C or Fortran will reduce the computation time dramatically, since the main bottleneck in MATLAB are the nested loops, which are hardly avoidable in MP2 calculations.

For the readers convenience, we briefly recall the grid-based method for factorized calculation of the TEI matrix B introduced in [25]. As in usual computational practice, the integration domain in (2.1) can be restricted to the finite bounding box $[-b, b]^3$. Introduce the uniform $n \times n \times n$ rectangular grid on $[-b, b]^3$, then each basis function $g_\mu(x)$ can be discretized by a three-dimensional tensor $\mathbf{G}_\mu = [g_\mu(x_1(i), x_2(j), x_3(k))]_{i,j,k=1}^n \in \mathbb{R}^{n \times n \times n}$, ($\mu = 1, \dots, N_b$), obtained by sampling of $g_\mu(x)$ over the midpoints $(x_1(i), x_2(j), x_3(k))$ of the grid-cells with index (i, j, k) .

Given the discretized basis function \mathbf{G}_μ , ($\mu = 1, \dots, N_b$), we assume without loss of generality that it is a rank-1 tensor, $\text{rank}(\mathbf{G}_\mu) = 1$, i.e. it is a separable data array $\mathbf{G}_\mu = G_\mu^{(1)} \otimes G_\mu^{(2)} \otimes G_\mu^{(3)} \in \mathbb{R}^{n \times n \times n}$, with the skeleton vectors $G_\mu^{(\ell)} \in \mathbb{R}^n$. Let

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

be the side matrix associated with a product-basis tensor

$$\mathbf{G} = [\mathbf{G}_{\mu\nu}] := [\mathbf{G}_\mu \odot \mathbf{G}_\nu]_{1 \leq \mu, \nu \leq N_b} \in \mathbb{R}^{n \times n \times n \times N_b^2},$$

where \odot denotes the Hadamard (pointwise) product of tensors. The matrix $G^{(\ell)}$ is composed (concatenated) by the skeleton vectors $G_\mu^{(\ell)} \odot G_\nu^{(\ell)} \in \mathbb{R}^n$ of \mathbf{G} in mode ℓ .

Introduce the rank- $R_{\mathcal{N}}$ canonical tensor $\mathbf{P}_{\mathcal{N}} = \sum_{k=1}^{R_{\mathcal{N}}} P_k^{(1)} \otimes P_k^{(2)} \otimes P_k^{(3)} \in \mathbb{R}^{n \times n \times n}$, approximating the 3D Newton kernel $\frac{1}{\|x\|}$, see [22], and denote by $P^{(\ell)} = [P_1^{(\ell)}, \dots, P_{R_{\mathcal{N}}}^{(\ell)}] \in \mathbb{R}^{n \times R_{\mathcal{N}}}$, $\ell = 1, 2, 3$, the related factor matrices. Now we are able to represent the TEI matrix B in the factorized form using a full set of convolved product basis functions. In fact, using the scalar product representation of $n \times n \times n$ arrays we rewrite the discretized integrals (2.1) in terms of tensor operations [25],

$$b_{\mu\nu\kappa\lambda} = \langle \mathbf{G}_{\mu\nu}, \mathbf{P}_{\mathcal{N}} * \mathbf{G}_{\kappa\lambda} \rangle_{n \otimes 3}, \quad (2.2)$$

where $*$ means the convolution product of tensors. Calculating the scalar products on rank-1 tensors (see Appendix A), and for each fixed multiindex, $\mu\nu\kappa\lambda$, we arrive at the new *tensor factorization* of B ,

$$B = \sum_{k=1}^{R_{\mathcal{N}}} \odot_{\ell=1}^3 G^{(\ell)T} (P_k^{(\ell)} *_n G^{(\ell)}). \quad (2.3)$$

Representation (2.3) can be implemented in the QTT format with logarithmic complexity in the grid variable provided that $n = 2^L$ (see Appendix B).

The improved factorization of the matrix B serves to minimize the number of convolution products in (2.1) that is $\frac{N_b(N_b+1)}{2}$, [25]. The approach is based on the truncated singular value decomposition (SVD) for finding the minimal set of dominating columns in the large site matrix $G^{(\ell)}$, $\ell = 1, 2, 3$, representing the full (and highly redundant) set of product basis functions sampled on a grid (see Algorithm 3 in Appendix B). Given a tolerance $\varepsilon > 0$, we compute the ε -truncated SVD-based left-orthogonal decomposition of $G^{(\ell)}$,

$$G^{(\ell)} \cong U^{(\ell)} V^{(\ell)T}, \quad \text{such that} \quad \|G^{(\ell)} - U^{(\ell)} V^{(\ell)T}\|_F \leq \varepsilon, \quad \ell = 1, 2, 3, \quad (2.4)$$

with orthogonal matrix $U^{(\ell)} \in \mathbb{R}^{n \times R_\ell}$ and a matrix $V^{(\ell)} \in \mathbb{R}^{N_b^2 \times R_\ell}$, where $U^{(\ell)}, V^{(\ell)}$ represent the so-called left and right redundancy-free (RF) basis sets.

Substitution of the side matrix decomposition (2.4) to (2.3) leads to the redundancy-free factorized ε -approximation of the matrix B ,

$$B = \sum_{k=1}^{R_{\mathcal{N}}} \odot_{\ell=1}^3 G^{(\ell)T} (P_k^{(\ell)} *_n G^{(\ell)}) \cong \sum_{k=1}^{R_{\mathcal{N}}} \odot_{\ell=1}^3 V^{(\ell)} M_k^{(\ell)} V^{(\ell)T} =: B_{\varepsilon}, \quad (2.5)$$

where $V^{(\ell)}$ represents the corresponding right RF basis, \odot denotes the point-wise (Hadamard) product of matrices, and

$$M_k^{(\ell)} = U^{(\ell)T} (P_k^{(\ell)} *_n U^{(\ell)}) \in \mathbb{R}^{R_{\ell} \times R_{\ell}}, \quad k = 1, \dots, R_{\mathcal{N}}, \quad (2.6)$$

stands for the Galerkin convolution matrix on the left RF basis, $U^{(\ell)}$, $\ell = 1, 2, 3$ (see Algorithm 4 in Appendix B). Equation (2.6) includes only $R_{\ell} \ll N_b^2$ convolution products.

Numerical experiments show that the Frobenius error of these rank decompositions decays exponentially in the rank parameter, R_{ℓ} ,

$$\|G^{(\ell)} - U^{(\ell)}V^{(\ell)T}\|_F \leq C e^{-\gamma_{\ell} R_{\ell}}, \quad \ell = 1, 2, 3, \quad \gamma_{\ell} > 0.$$

Figure 2.1 illustrates the exponential decay in singular values of $G^{(\ell)}$ for several moderate size molecules.

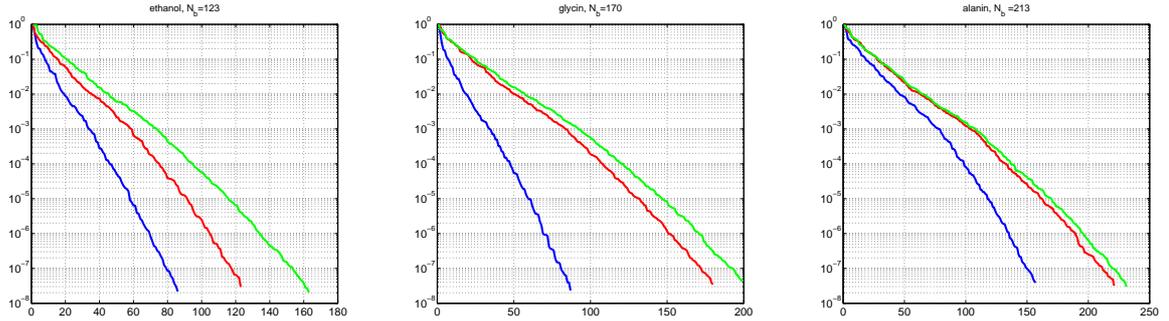


Figure 2.1: Singular values of $G^{(\ell)}$ for $\ell = 1, 2, 3$: NH_3 (left), $\text{C}_2\text{H}_5\text{OH}$ (middle) and glycine (right) molecules, with the numbers N_b, N_{orb} equal to 48, 5; 123, 13 and 170, 20, respectively.

The Hartree-Fock calculations for the moderate size molecules are usually based on the incomplete Cholesky decomposition [29, 30, 31] applied to the symmetric and positive definite TEI matrix B ,

$$B \approx LL^T, \quad L \in \mathbb{R}^{N_b^2 \times R_B}, \quad (2.7)$$

where the separation rank $R_B \ll N_b^2$ is of order $O(N_b)$. This decomposition can be efficiently computed by using the precomputed (off-line step) factorization of B as in (2.5), that requires only a small number of adaptively chosen column vectors in B , [25]. The detailed computational scheme is presented in Algorithm 1 below.

The results of our numerical experiments using Matlab implementation of Algorithm 1 indicate that the truncated Cholesky decomposition with the separation rank $O(N_b)$ ensures the satisfactory numerical precision $\varepsilon > 0$ of order $10^{-5} - 10^{-6}$. The refined rank estimate

Algorithm 1 Truncated Cholesky factorization of the matrix $B \in \mathbb{R}^{N \times N}$, $N = N_b^2$

Input: Right RF basis $V^{(\ell)}$; set of $R_\ell \times R_\ell$ matrices $M_k^{(\ell)}$ for $\ell = 1, 2, 3$, $k = 1, \dots, R_{N_\ell}$, error tolerance $\varepsilon > 0$.

(1) Compute the diagonal $b = \text{diag}(B)$: $B(i, i) = \sum_{k=1}^{R_{N_\ell}} \odot_{\ell=1}^3 V^{(\ell)}(i, :) M_k^{(\ell)} V^{(\ell)}(:, i)^T$;

(2) Set $r = 1$, $\text{err} = \|b\|_1$ and initialize $\pi = \{1, \dots, N\}$;

While $\text{err} > \varepsilon$ perform (3) - (9)

(3) Find $m = \text{argmax}\{b(\pi_j) : j = r, r + 1, \dots, N\}$; update π by swapping π_r and π_m ;

(4) Set $\ell_{r, \pi_r} = \sqrt{b(\pi_r)}$;

For $r + 1 \leq m \leq N$ perform (5) - (7)

(5) Compute the entire column of B via $B(:, r) = \sum_{k=1}^{R_{N_\ell}} \odot_{\ell=1}^3 V^{(\ell)} M_k^{(\ell)} V^{(\ell)}(:, r)^T$;

(6) Compute the L-column $\ell_{r, \pi_m} = (B(r, \pi_m) - \sum_{j=1}^{r-1} \ell_{j, \pi_r} \ell_{j, \pi_m})$;

(7) Update the stored diagonal $b(\pi_m) = b(\pi_m) - \ell_{r, \pi_m}^2$;

(8) Compute $\text{err} = \sum_{j=r+1}^N b(\pi_j)$;

(9) Increase $r = r + 1$;

Output: Low-rank decomposition of B , $B_\varepsilon = LL^T$, such that $\text{tr}(B - B_\varepsilon) \leq \varepsilon$.

$O(N_b |\log \varepsilon|)$ was observed in numerical experiments for every molecular system we calculated so far.

Finally, we notice that the redundancy-free factorization (2.5) can be viewed as the algebraic tensor-structured counterpart of the *density fitting scheme* commonly used in quantum chemistry [2]. In our approach the "one-dimensional density fitting" independently for each space dimension reduces the ε -ranks of the dominating directional bases to the lowest possible value. The robust error control in the proposed basis optimization method is based on the low-rank approximation by purely algebraic SVD-like procedure that allows to eliminate the redundancy in the product basis set up to given precision $\varepsilon > 0$.

3 MP2 correction by multiple tensor factorizations

3.1 Tensor-structured representation of basic quantities

The various degrees Møller-Plesset perturbation theory (in particular, second-order MP2 model) significantly improves the HF correlation energy and other molecular characteristics in the case of large basis sets [13]. However, the numerical payoff of the straightforward implementation scales as $O(N_b^5)$. Here we describe the main ingredients of our computational scheme that reduces this cost by using low-rank tensor decompositions of arising multidimensional data arrays.

Let $C = \{C_{\mu i}\} \in \mathbb{R}^{N_b \times N_b}$ be the coefficient matrix representing the Hartree-Fock molecular orbitals (MO) in the atomic orbitals (AO) basis set $\{g_\mu\}_{1 \leq \mu \leq N_b}$, and obtained in the Hartree-Fock calculations. First, one has to transform the TEI tensor $\mathbf{B} = [b_{\mu\nu\lambda\sigma}]$, computed in the initial AO basis set, to that represented in the MO basis,

$$\mathbf{V} = [v_{iajb}] : \quad v_{iajb} = \sum_{\mu, \nu, \lambda, \sigma=1}^{N_b} C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b} b_{\mu\nu\lambda\sigma}, \quad a, b \in I_{vir}, \quad i, j \in I_{occ},$$

where $I_{occ} := \{1, \dots, N_{orb}\}$, $I_{vir} := \{N_{orb} + 1, \dots, N_b\}$, with N_{orb} denoting the number of occupied orbitals. In the following, we shall use the notation

$$N_{vir} = N_b - N_{orb}, \quad N_{ov} = N_{orb}N_{vir}.$$

Straightforward computation of the tensor \mathbf{V} in above representation makes the dominating impact to the overall numerical cost of MP2 calculations, $O(N_b^5)$.

Given the tensor $\mathbf{V} = [v_{iajb}]$, the second order MP2 perturbation to the HF energy is calculated by

$$E_{MP2} = - \sum_{a,b \in I_{vir}} \sum_{i,j \in I_{occ}} \frac{v_{iajb}(2v_{iajb} - v_{ibja})}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \quad (3.1)$$

where the real numbers ε_k , $k = 1, \dots, N_b$, represent the HF eigenvalues. Notice that the denominator in (3.1) remains strongly positive if $\varepsilon_a > 0$ for $a \in I_{vir}$ and $\varepsilon_i < 0$ for $i \in I_{occ}$. The latter conditions (nonzero homo lumo gap) will be assumed in the following.

Introducing the so-called doubles amplitude tensor \mathbf{T} ,

$$\mathbf{T} = [t_{iajb}] : \quad t_{iajb} = \frac{(2v_{iajb} - v_{ibja})}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \quad a, b \in I_{vir}; i, j \in I_{occ},$$

the MP2 perturbation takes the form of a simple scalar product of tensors,

$$E_{MP2} = -\langle \mathbf{V}, \mathbf{T} \rangle = -\langle \mathbf{V} \odot \mathbf{T}, \mathbf{1} \rangle,$$

where the summation is restricted to the subset of indices

$$\mathcal{I} := (I_{vir} \times I_{occ}) \times (I_{vir} \times I_{occ}) \subset I_b^{\otimes 4},$$

and $\mathbf{1}$ denotes the rank-1 all-ones tensor. Define the reciprocal ‘‘energy’’ tensor

$$\mathbf{E} = [e_{abij}] := \left[\frac{1}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \right], \quad a, b \in I_{vir}; i, j \in I_{occ}, \quad (3.2)$$

and the partly transposed tensor (transposition in indices a and b)

$$\mathbf{V}' = [v'_{iajb}] := [v_{ibja}].$$

Then the doubles amplitude tensor \mathbf{T} will be further decomposed as

$$\mathbf{T} = \mathbf{T}^{(1)} + \mathbf{T}^{(2)} = 2\mathbf{V} \odot \mathbf{E} - \mathbf{V}' \odot \mathbf{E}. \quad (3.3)$$

Each term in the right-hand side above will be treated separately.

3.2 Separation rank estimates and numerical illustrations

In this section we show that the rank $R_B = O(N_b)$ approximation to the symmetric TEI matrix $B \approx LL^T$, with the Cholesky factor $L \in \mathbb{R}^{N \times R_B}$, allows to introduce the low-rank representation of the tensor \mathbf{V} and the R_B -term decomposition of \mathbf{T} , and then to reduce the asymptotic complexity of MP2 calculations to $O(N_b^3 N_{orb})$, and even further.

Lemma 3.1 *Given the rank- R_B Cholesky decomposition of the matrix B , the matrix unfolding $V = [v_{ia;jb}]$ allows a rank decomposition with rank $\leq R_B$. Moreover, the tensor $\mathbf{V}' = [v_{ibja}]$ enables an R_B -term decomposition of mixed form.*

Proof. Let us denote by $L_k = L_k(\mu; \nu)$, $k = 1, \dots, R_B$, a matrix unfolding of the vector $L(:, k) \in \mathbb{R}^{N_b \times N_b}$ in the Cholesky factor $L \in \mathbb{R}^{N_b^2 \times R_B}$, and notice that the Cholesky factorization can be written pointwise in a form

$$b_{\mu\nu;\lambda\sigma} \approx \sum_{k=1}^{R_B} L_k(\mu; \nu) L_k(\sigma; \lambda).$$

Let $C_m = C(:, m)$, $m = 1, \dots, N_b$ be the m -th column of the coefficient matrix $C = \{C_{\mu i}\} \in \mathbb{R}^{N_b \times N_b}$. Then, the rank- R_B representation of the matrix unfolding $V = [v_{ia;jb}] \in \mathbb{R}^{N_{ov} \times N_{ov}}$ takes a form

$$V = L_V L_V^T, \quad L_V \in \mathbb{R}^{N_{ov} \times R_B},$$

where

$$L_V((i-1)N_{vir} + a; k) = C_i^T L_k C_a, \quad k = 1, \dots, R_B, \quad a = 1, \dots, N_{vir}, \quad i = 1, \dots, N_{orb}.$$

This is justified by the following transformations

$$\begin{aligned} v_{iajb} &= \sum_{\mu, \nu, \lambda, \sigma=1}^{N_b} C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b} b_{\mu\nu\lambda\sigma} \\ &\approx \sum_{k=1}^{R_B} \sum_{\mu, \nu, \lambda, \sigma=1}^{N_b} C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b} L_k(\mu; \nu) L_k(\sigma; \lambda) \\ &= \sum_{k=1}^{R_B} \left(\sum_{\mu, \nu=1}^{N_b} C_{\mu i} C_{\nu a} L_k(\mu; \nu) \right) \left(\sum_{\lambda, \sigma=1}^{N_b} C_{\lambda j} C_{\sigma b} L_k(\sigma; \lambda) \right) \\ &= \sum_{k=1}^{R_B} (C_i^T L_k C_a) (C_b^T L_k^T C_j). \end{aligned} \tag{3.4}$$

This proves the first statement. Furthermore, the partly transposed tensor $\mathbf{V}' := [v_{ibja}]$ allows a R_B -term decomposition derived similar to (3.4),

$$v'_{iajb} = v_{ibja} = \sum_{k=1}^{R_B} (C_i^T L_k C_b) (C_a^T L_k^T C_j). \tag{3.5}$$

This completes our proof ■

It is necessary to compute and store the only L_V factor in the above symmetric factorizations of V and V' , hence, the storage cost of decompositions (3.4) and (3.5) restricted to the active index set $I_{vir} \times I_{occ}$ amounts to $R_B N_{vir} N_{orb}$ numbers. The complexity of straightforward computation can be estimated by $O(R_B N_b^2 N_{orb})$.

Next, we consider separable representation of the tensor \mathbf{T} in (3.3). To that end, we first apply low-rank canonical ε -approximation to the tensor \mathbf{E} . The following lemma describes the canonical approximation to the tensor \mathbf{E} that converges exponentially fast in the rank parameter.

Lemma 3.2 Suppose that the so-called homo lumo gap is estimated by

$$\min_{a \in I_{vir}, i \in I_{occ}} |\varepsilon_a - \varepsilon_i| \geq \frac{\delta}{2} > 0.$$

Then the rank- R_E , $R_E = 2M + 1$, canonical approximation to the tensor $\mathbf{E} \approx \mathbf{E}_{R_E}$,

$$e_{a,b,i,j} \approx \sum_{p=-M}^M c_p e^{-\alpha_p(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)}, \quad \alpha_p > 0, \quad (3.6)$$

with the particular choice $h = \pi/\sqrt{M}$, $\alpha_p = e^{ph}$, $c_p = h\alpha_p$ and $M = O(|\log \varepsilon \log \delta|)$, provides the error bound

$$\|\mathbf{E} - \mathbf{E}_{R_E}\|_F \leq O(\varepsilon).$$

Proof. Consider the sinc-quadrature approximation of the Laplace transform applied to the 4th order Hilbert tensor,

$$\frac{1}{x_1 + x_2 + x_3 + x_4} = \int_0^\infty e^{-t(x_1+x_2+x_3+x_4)} dt \approx \sum_{k=-M}^M c_k e^{-t_k(x_1+x_2+x_3+x_4)},$$

for $x_i \geq 0$, $\sum x_i > \delta$, that converges exponentially fast in M , see [32, 33]. This proves the statement. \blacksquare

It is worth to note that the matrix V exhibits an exponential decay in the singular values (observed in numerical experiments, see Fig. 3.1) which means that the approximation error $\varepsilon > 0$ can be achieved with the separation rank $R_V = O(|\log \varepsilon|)$.

Figure 3.1 illustrates the exponential convergence in the rank parameter for the low-rank decompositions of matrices V and $E = [e_{ab;ij}]$.

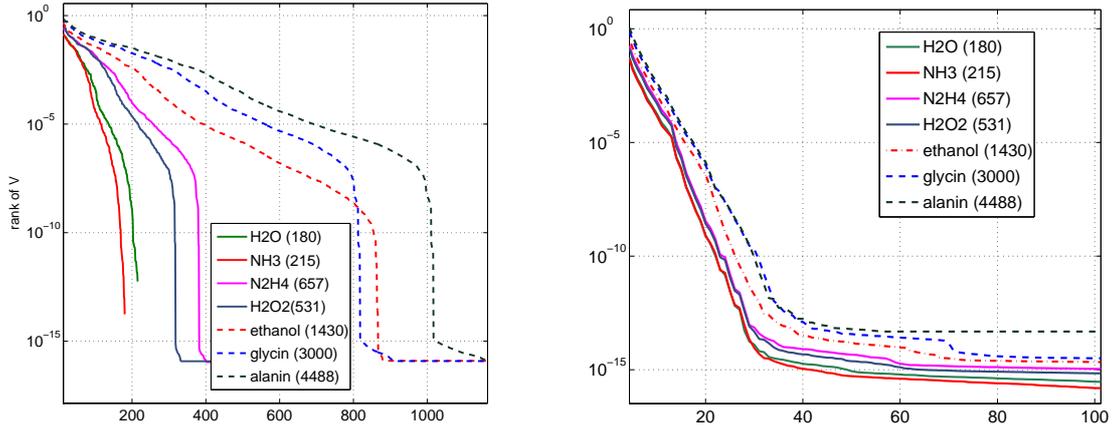


Figure 3.1: Singular values of matrix unfolding V (left) and E (right) for some compact molecules, including the aminoacids glycine ($C_2H_5NO_2$) and alanine ($C_3H_7NO_2$). Numbers in brackets indicate the size of a matrix, that is $N_{orb}N_{virt}$, for the corresponding molecule.

3.3 Complexity bounds, sketch of algorithm, QTT compression

Lemmas 3.1 and 3.2 result in the following complexity bound: The Hadamard product $\mathbf{V} \odot \mathbf{T}$, as well as the resultant functional E_{MP2} , can be evaluated at the expense $O(R_E R_B^2 N_{occ} N_{vir})$. In fact, the first term in a splitting $\mathbf{T} = \mathbf{T}^{(1)} + \mathbf{T}^{(2)}$ is represented by

$$\mathbf{T}^{(1)} = 2\mathbf{V} \odot \mathbf{E} = 2[t_{iajb}^{(1)}],$$

where

$$t_{iajb}^{(1)} = \sum_{p=1}^{R_E} c_p \sum_{k=1}^{R_B} (e^{\alpha_p \varepsilon_i} C_i^T L_k e^{-\alpha_p \varepsilon_a} C_a) (e^{-\alpha_p \varepsilon_b} C_b^T L_k^T e^{\alpha_p \varepsilon_j} C_j), \quad (3.7)$$

such that $L_k = L_k(:, :)$ stands for the $N_b \times N_b$ matrix unfolding of the Cholesky vector $L(:, k)$. Then the numerical complexity of this rank- $(R_E R_B)$ approximation is estimated via the multiple of R_E with the corresponding cost for the treatment of the tensor \mathbf{V} , that is $O(R_E R_B N_{occ} N_{vir})$. Furthermore, the R_B -term decomposition of $\mathbf{V}' := [v_{ibja}]$, see (3.5), again leads to the summation over $(R_E R_B)$ -term representation of the second term in the splitting of \mathbf{T} ,

$$\mathbf{T}^{(2)} = [t_{iajb}^{(2)}] = \mathbf{V}' \odot \mathbf{E},$$

where

$$t_{iajb}^{(2)} = \sum_{p=1}^{R_E} c_p \sum_{k=1}^{R_B} (e^{\alpha_p \varepsilon_i} C_i^T L_k e^{-\alpha_p \varepsilon_a} C_b) (e^{-\alpha_p \varepsilon_b} C_a^T L_k^T e^{\alpha_p \varepsilon_j} C_j). \quad (3.8)$$

Based on the rank decompositions of the matrix B , the energy tensor \mathbf{E} , and of the doubles amplitude tensor \mathbf{T} , we utilize the final Algorithm 2 to compute the MP2 energy correction.

Algorithm 2 Fast tensor-structured computation of the MP2 energy correction

Input: Rank- R_B factorization LL^T of B , coefficient matrix C , and Hartree-Fock eigenvalues, $\varepsilon_1, \dots, \varepsilon_{N_b}$, error tolerance $\varepsilon > 0$.

(1) Compute the column vectors in the rank- R_B decomposition of matrix $V = [v_{ia;jb}]$, $C_i^T L_k C_a$, $k = 1, \dots, R_B$ ($i, a = 1, \dots, N_b$) as in (3.4).

(2) Precompute the matrix factors in R_B -term decomposition of $V' = [v_{ib;j a}]$ as in (3.5).

(3) Construct the canonical decomposition of "energy" tensor $\mathbf{E} = [e_{a,b,i,j}]$ by the sinc-quadrature (3.6), $e_{a,b,i,j} \approx \sum_{p=-M}^M c_p e^{-\alpha_p (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)}$, as in Lemma 3.2.

(4) Compute a tensor $\mathbf{T}^{(1)} = 2\mathbf{V} \odot \mathbf{E}$ as in (3.7) using rank decompositions of V and \mathbf{E} .

(5) Compute a tensor $\mathbf{T}^{(2)} = \mathbf{V}' \odot \mathbf{E}$ as in (3.8) using rank decompositions of V' and \mathbf{E} .

(6) Compute the MP2 correction by "formatted" scalar product $E_{MP2} = -\langle \mathbf{V}, \mathbf{T}^{(1)} + \mathbf{T}^{(2)} \rangle$.

Output: MP2 energy correction E_{MP2} .

Table 3.1 represents the effect of MP2 correction for several compact molecules. In most cases this correction amounts to about 0.4% of the total energy.

The tensor-structured factorizations of the matrix B makes it possible to reduce the overall cost to $O(N_b^2 N_{vir} N_{orb})$ by using the QTT approximation of the long column vectors in the Cholesky factor L . Figure 5.1 (Left) in Appendix B indicates that the average QTT ranks

Molecules	H ₂ O	H ₂ O ₂	N ₂ H ₄	C ₂ H ₅ OH	C ₂ H ₅ NO ₂	C ₃ H ₇ NO ₂
$N_b; N_{orb}$	41, 5	68, 9	82, 9	123, 13	170, 20	211, 24
E_0	-76.0308	-150.7945	-111.1897	-154.1006	-282.8651	-321.9149
E_{MP2}	-0.2587	-0.4927	-0.4510	-0.6257	-1.0529	-1.24

Table 3.1: MP2 correction to the ground state energy (in hartree) for some compact molecules, including aminoacids glycine (C₂H₅NO₂) and alanine (C₃H₇NO₂).

of columns vectors in the Cholesky factor and of the vectorized density matrix $C \in \mathbb{R}^{N_b \times N_b}$ remains to be almost the same (depend only on the entanglement properties of a molecule) and they can be described quite precisely by the estimate

$$\text{rank}_{QTT}(L(:, k)) \approx \text{rank}_{QTT}(C_k) \leq 3N_{orb}, \quad k = 1, \dots, N_B.$$

This hidden structural property implies that the computation and storage cost for the matrix $V = L_V L_V^T$, involved in Algorithm 2 (the most expensive part of the MP2 calculation) can be reduced to $O(N_{orb}^2)$ at the main step in (3.4), $C_i^T L_k C_a$, instead of N_b^2 , indicating the reduced redundancy in the AO basis in the case of compact molecules.

Further reduction of the numerical complexity can be based on the more specific properties of the matrix unfolding V when using a physical insight to the problem (say, flat or extended molecules, multiple symmetries, periodic structures, accounting data sparsity, etc.).

4 Appendix A: Introduction to tensor calculus

In this section we sketch the main ingredients in the multilinear algebra of tensors applied in the present paper (see also the literature surveys [34, 35, 36, 37]). Tensor of order d is defined as a multidimensional array with a d -tuple index set,

$$\mathbf{A} = [a_{i_1, \dots, i_d}] \in \mathbb{R}^{n_1 \times \dots \times n_d} \quad \text{with} \quad i_\ell \in I_\ell := \{1, \dots, n_\ell\},$$

considered as an element of a linear vector space equipped with the Euclidean scalar product. Tensors with all dimensions having equal size $n_\ell = n$, $\ell = 1, \dots, d$, will be called an $n^{\otimes d}$ tensor. The required storage size scales exponentially in the dimension, n^d , (the so-called "curse of dimensionality").

To get rid of exponential scaling in the dimension, one can apply the rank-structured separable representations (approximations) of multidimensional tensors. The simplest rank structured ansatz, is given by the *tensor product* of vectors $u^{(\ell)} = \{u_{i_\ell}^{(\ell)}\}_{i_\ell \in I_\ell} \in \mathbb{R}^{I_\ell}$ ($\ell = 1, \dots, d$) that forms the canonical rank-1 tensor,

$$\mathbf{A} = u^{(1)} \otimes \dots \otimes u^{(d)} \in \mathbb{R}^{n_1 \times \dots \times n_d} \quad \text{with entries} \quad u_{i_1, \dots, i_d} = u_{i_1}^{(1)} \dots u_{i_d}^{(d)},$$

requiring only dn numbers to store it. A tensor in the R -term canonical format is defined as

$$\mathbf{A} = \sum_{k=1}^R c_k u_k^{(1)} \otimes \dots \otimes u_k^{(d)}, \quad c_k \in \mathbb{R}, \quad (4.1)$$

where $u_k^{(\ell)}$ are normalized vectors, and R is called the canonical rank of a tensor.

Given the rank parameter $\mathbf{r} = (r_1, \dots, r_d)$, the multidimensional tensor \mathbf{A} is represented in the rank- \mathbf{r} Tucker format if

$$\mathbf{A} = \sum_{\nu_1=1}^{r_1} \cdots \sum_{\nu_d=1}^{r_d} \beta_{\nu_1, \dots, \nu_d} v_{\nu_1}^{(1)} \otimes \cdots \otimes v_{\nu_d}^{(d)},$$

with the set of orthonormal vectors $v_{\nu_\ell}^{(\ell)} \in \mathbb{R}^{I_\ell}$ ($1 \leq \nu_\ell \leq r_\ell$) for $\ell = 1, \dots, d$. The coefficients tensor $\boldsymbol{\beta} = [\beta_{\nu_1, \dots, \nu_d}]$ is called the core tensor (usually, for function related tensors we have $r = \max_{\ell} \{r_\ell\} = O(\log n) \ll n$, [38]).

The canonical and Tucker decomposition have been since long used in the computer science for the quantitative analysis of correlations in the multidimensional arrays in data processing and chemometrics, see [34] and references therein.

The exceptional properties of the Tucker decomposition for the approximation of discretized multidimensional functions have been revealed in [38, 39], where it was proven that for a class of function-related tensors the approximation error of the Tucker decomposition *decays exponentially* with respect to the Tucker rank. The canonical-to-Tucker decomposition was introduced in [39, 40] as an efficient and robust tool for reducing the canonical rank of 3D function related tensors.

Rank-structured tensor representation provides fast multi-linear algebra with linear complexity scaling in the dimension d . For example, for given canonical tensors $\mathbf{A}_1, \mathbf{A}_2$, the Euclidean scalar product can be computed by

$$\langle \mathbf{A}_1, \mathbf{A}_2 \rangle := \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} c_k b_m \prod_{\ell=1}^d \langle u_k^{(\ell)}, v_m^{(\ell)} \rangle,$$

at the expense $O(dnR_1R_2)$. The Hadamard product of tensors $\mathbf{A}_1, \mathbf{A}_2$ given in the canonical format (4.1) is calculated in $O(dnR_1R_2)$ operations by

$$\mathbf{A}_1 \odot \mathbf{A}_2 := \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} c_k b_m \left(u_k^{(1)} \odot v_m^{(1)} \right) \otimes \cdots \otimes \left(u_k^{(d)} \odot v_m^{(d)} \right).$$

In electronic structure calculations, the three-dimensional convolution transform with the Newton convolving kernel, $\frac{1}{\|x-y\|}$, is one of the most computationally expensive operations. The tensor method to compute this transform over large $n \times n \times n$ Cartesian grids in $O(n \log n)$ complexity was introduced in [22]. Given canonical rank- R_1 (resp. rank- R_2) tensors $\mathbf{A}_1, \mathbf{A}_2$ in a form (4.1), their convolution product is represented by the sum of tensor products of 1D convolutions,

$$\mathbf{A}_1 * \mathbf{A}_2 = \sum_{k=1}^{R_1} \sum_{m=1}^{R_2} c_k b_m \left(u_k^{(1)} * v_m^{(1)} \right) \otimes \left(u_k^{(2)} * v_m^{(2)} \right) \otimes \left(u_k^{(3)} * v_m^{(3)} \right), \quad (4.2)$$

where $u_k^{(\ell)} * v_m^{(\ell)}$ denotes the convolution product of n -vectors. The numerical cost of tensor convolution in both storage and time is estimated by $O(R_1 R_2 n \log n)$. Hence, it considerably outperforms the conventional 3D FFT-based algorithm of the complexity $O(n^3 \log n)$, for large enough n , as shown by numerics in [40].

In tensor-structured numerical methods the calculation of the $3D$ convolution integrals is replaced by a sequence of $1D$ scalar and Hadamard products, and $1D$ convolution transforms [40, 21]. However, the multilinear tensor operations in above mentioned formats mandatory lead to increase of tensor ranks which can be reduced by the canonical-to-Tucker and Tucker-to-canonical algorithms introduced in [22, 39, 40].

For the problems in higher dimensions, the low-parametric rank-structured tensor representation of functions can be based on the commonly used matrix-product states (MPS) [41, 42] and equivalently tensor train (TT) [43] formats.

For a given rank parameter $\mathbf{r} = (r_1, \dots, r_{d-1})$, and the respective index sets $J_\ell = \{1, \dots, r_\ell\}$ ($\ell = 1, \dots, d-1$), the rank- \mathbf{r} tensor train format contains all elements $\mathbf{A} = [a(i_1, \dots, i_d)]$ in $\mathbb{W}_{\mathbf{n}} = \mathbb{R}^{n_1 \times \dots \times n_d}$ that can be represented as the chain of contracted products of 3-tensors over the d -fold product index set $J := \times_{\ell=1}^{d-1} J_\ell$,

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

In the compact form, we have the entry-wise MPS-type matrix factorization (that explains the original name matrix product states),

$$a(i_1, i_2, \dots, i_d) = A_{i_1}^{(1)} A_{i_2}^{(2)} \cdots A_{i_d}^{(d)}, \quad (4.3)$$

where each $A_{i_k}^{(k)} = G^{(k)}(\alpha_{k-1}, i_k, \alpha_k)$ is $r_{k-1} \times r_k$ matrix depending on i_k with the convention $r_0 = r_d = 1$.

The TT representation reduces the storage complexity of $n^{\otimes d}$ tensor to $O(dr^2n)$, $r = \max r_k$. The important multilinear algebraic operations on TT tensors can be implemented with linear complexity scaling in n and d . For example, the scalar product of TT tensors $\langle \mathbf{A}, \mathbf{B} \rangle$ amounts to $O(dr^3n) \ll n^d$ operations.

The $O(d \log n)$ -quantics approximation method introduced in 2009³ (see [28]) provides a simple and powerful tool to compress function-related vectors (or tensors) by using the TT-approximation on quantized images (quantics-TT or QTT).

The QTT representation of functional vectors of size $n = 2^L$ needs only

$$2 \cdot L \cdot k^2 \ll 2^L$$

numbers, where k is the QTT-separation rank, providing a significant reduction of the storage and computational complexity. In [28] it was proven that the rank parameter k in the QTT approximation is negligibly small for a wide class of discretized functions: $k = 1$ for complex exponents, $k = 2$ for trigonometric functions and for Chebyshev polynomial on Chebyshev-Gauss-Lobatto grid, $k \leq m + 1$ for polynomials of degree m , while k is a small constant for wavelet basis functions, etc.

To sketch the idea, we suppose that $n = 2^L$ with some $L = 1, 2, \dots$, then next definition introduces the quantization of $n^{\otimes d}$ tensors into the elements of auxiliary D -dimensional tensor space with $D = d \log_2 n$. For $d = 1$, The respective binary folding of degree L ,

³B. Khoromskij, *O(d log N)-Quantics Approximation of N-d Tensors in High-Dimensional Numerical Modeling*. Preprint 55/2009, Max-Planck Institute for Mathematics in the Sciences, Leipzig 2009. <http://www.mis.mpg.de/publications/preprints/2009/prepr2009-55.html>

reshapes the initial n -vector $\mathbf{X} = [X(i)]_{i \in I} \in \mathbb{R}^n$, to the element $\mathbf{Y} \in \bigotimes_{\nu=1}^L \mathbb{K}^2$, $\mathbb{K} \in \{\mathbb{R}, \mathbb{C}\}$ by

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

with $j_\nu \in \{1, 2\}$ for $\nu = 1, \dots, L$. 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 $i - 1$,

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

The quantized approximation method now applies to the L -dimensional tensor \mathbf{Y} , that can be represented in the canonical or TT format (QTT approximation).

The construction for $d \geq 2$, as well as in the general case $n = q^L$, $q = 2, 3, \dots$, is presented in [28].

The QTT approximation method allows to represent a class of matrices in low QTT rank format [44, 45] as well as to implement the multidimensional FFT and convolution transforms with logarithmic complexity scaling, $O(\log n)$, [46, 47].

5 Appendix B: On redundancy free factorization of B

First, we describe the efficient scheme to compute the low-rank decomposition of the site matrix $G^{(\ell)}$ introduced in (2.4). The direct SVD of rectangular matrices $G^{(\ell)} \in \mathbb{R}^{n \times N_b^2}$ can be prohibitive even for the moderate size molecules ($n \geq 2^{13}$, $N_b \geq 200$). To get rid of this difficulty, we adapt the five-step algorithm of the reduced computational and storage costs (Algorithm 3) to compute the low-rank approximation $G^{(\ell)} \cong U^{(\ell)} V^{(\ell)T}$ with the guaranteed tolerance $\varepsilon > 0$.

Algorithm 3 Fast low-rank ε -approximation of $G^{(\ell)}$

Input: rectangular matrices $G^{(\ell)} \in \mathbb{R}^{n \times N_b^2}$, $\ell = 1, 2, 3$, tolerance $\varepsilon > 0$.

(1) Find the factor $\tilde{U}^{(\ell)} \in \mathbb{R}^{n \times \tilde{R}_\ell}$ of the truncated Cholesky decomposition to the Gram-matrix $G^{(\ell)} G^{(\ell)T} \approx \tilde{U}^{(\ell)} (\tilde{U}^{(\ell)})^T$ by ε -thresholding of the diagonal elements.

(2) Orthogonalize the column space of $\tilde{U}^{(\ell)}$ by QR decomposition, $\tilde{U}^{(\ell)} := U^{(\ell)} R_U$.

(3) Project the initial matrix onto $U^{(\ell)}$, $\tilde{V}^{(\ell)} := G^{(\ell)T} U^{(\ell)}$ (can be executed in the data-sparse formats, say in QTT).

(4) QR decomposition $\tilde{V}^{(\ell)} := V^{(\ell)} R_V$, to obtain the orthogonal Q-factor $V^{(\ell)}$.

(5) Rank reduction (\tilde{R}_ℓ to R_ℓ) by SVD of $R_V \in \mathbb{R}^{\tilde{R}_\ell \times \tilde{R}_\ell}$; update $U^{(\ell)}$ and $V^{(\ell)}$.

Output: Rank- R_ℓ decomposition of $G^{(\ell)} \approx U^{(\ell)} V^{(\ell)T}$, with the orthogonal matrix $U^{(\ell)}$.

Step (3) in Algorithm 3 requires an access to the full matrix $G^{(\ell)}$. However, in the case when this matrix allows data-sparse representation, the respective matrix-vector multiplications can be implemented with the reduced cost. For example, given the low-rank QTT representation of the column vectors in $G^{(\ell)}$, the matrix-matrix product at Step (3) can be implemented in $O(N_b^2 R_\ell \log n)$ operations. Notice that the QTT ranks of the column vectors are estimated by $O(1)$ for all molecular systems considered so far. Another advantageous

feature is due to perfect parallel structure of the matrix-vector multiplication procedure at Step (3).

The following Algorithm 4 represents the main steps in the factorization scheme (2.5) – (2.6). Inspection of Algorithm 4 shows that the storage demand for representations (2.5)

Algorithm 4 Redundancy-free factorized ε -approximation to the matrix B

Input: Rank- R_ℓ decompositions $G^{(\ell)} \approx U^{(\ell)}V^{(\ell)T}$, factor matrices $P^{(\ell)} = [P_1^{(\ell)}, \dots, P_{R_{\mathcal{N}}}^{(\ell)}] \in \mathbb{R}^{n \times R_{\mathcal{N}}}$, $\ell = 1, 2, 3$, in the rank- $R_{\mathcal{N}}$ canonical Newton tensor $\mathbf{P}_{\mathcal{N}} \in \mathbb{R}^{n \times n \times n}$.

(1) For $\ell = 1, 2, 3$, compute convolution products $P_k^{(\ell)} *_n U^{(\ell)} \in \mathbb{R}^{n \times R_\ell}$, $k = 1, \dots, R_{\mathcal{N}}$.

(2) For $\ell = 1, 2, 3$, compute and store Galerkin projections onto the left RF directional basis: $M_k^{(\ell)} = U^{(\ell)T}(P_k^{(\ell)} *_n U^{(\ell)}) \in \mathbb{R}^{R_\ell \times R_\ell}$.

Output: Right RF basis $V^{(\ell)}$; set of $R_\ell \times R_\ell$ matrices $M_k^{(\ell)}$ for $\ell = 1, 2, 3$, $k = 1, \dots, R_{\mathcal{N}}$.

and (2.6) can be estimated by $R_{\mathcal{N}} \sum_{\ell=1}^3 R_\ell^2 + N_b^2 \sum_{\ell=1}^3 R_\ell$ and $O((R_G + R_{\mathcal{N}})n)$, respectively.

Further storage reduction can be achieved by the quantized-TT (QTT) approximation of the column vectors in $U^{(\ell)}$ and $V^{(\ell)}$ in (2.6). Specifically, the required storage amounts to $O((R_G + R_{\mathcal{N}}) \log n)$ reals. Figure 5.1 illustrates QTT-ranks behaviour for skeleton vectors in factorization (2.5) for some compact molecules with different number of electron orbitals N_{orb} (for QTT representation we used the TT-Toolbox 2.2⁴).

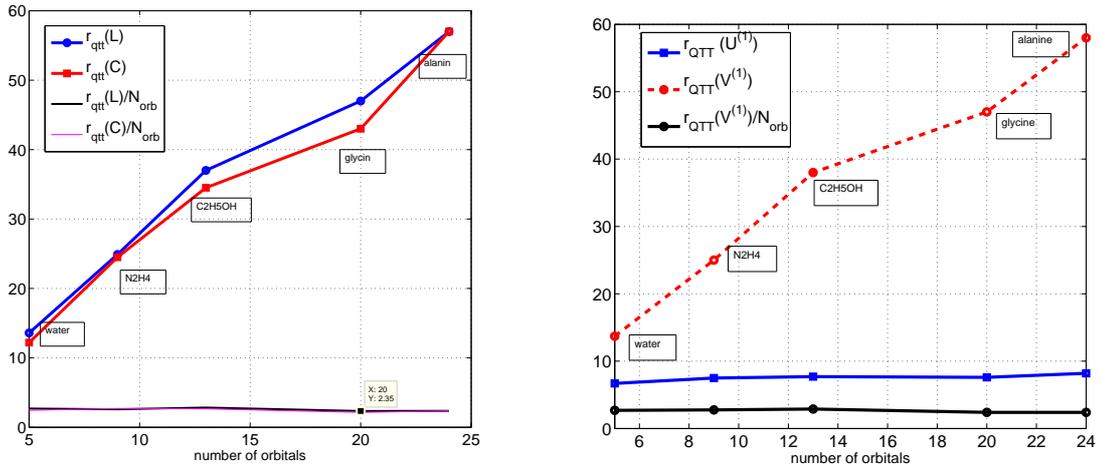


Figure 5.1: (Left): Average QTT ranks of the column vectors in L ($r_{QTT}(L)$), and in the vectorized coefficient matrix ($r_{QTT}(C)$) for several compact molecules. The "constant" lines at the level $2.35 \div 2.85$ indicate the corresponding ratios ($r_{QTT}(L)/N_{orb}$ and $r_{QTT}(C)/N_{orb}$) for the respective molecule. (Right): QTT ranks of skeleton vectors in factorization (2.5) – (2.6) for H₂O, N₂H₄, C₂H₅OH, C₂H₅NO₂ (glycine), C₃H₇NO₂ (alanine) calculations, with N_{orb} equal to 5, 9, 13, 20, and 24, respectively.

In some cases the representation may provide the direct low-rank decomposition of the matrix B . In fact, suppose that $R_\ell \leq C_\ell |\log \varepsilon| N_{orb}$, with constants $C_\ell \leq 1$, $\ell = 1, 2, 3$. Then

⁴Free download from <http://github.com/oseledets/TT-Toolbox>, INM RAS, Moscow.

the ε -rank of the matrix B is bounded by

$$\text{rank}(B_\varepsilon) \leq \min\{N_b^2, R_{\mathcal{N}}|\log \varepsilon|^3 N_{orb}^3 \prod_{\ell=1}^3 C_\ell\}. \quad (5.1)$$

Indeed, in accordance to [25] the rank estimate holds $\text{rank}(B_\varepsilon) \leq \min\{N_b^2, R_{\mathcal{N}}\prod_{\ell=1}^3 R_\ell\}$, which proves the statement.

Rank estimate (5.1) outlines the way to efficient implementation of (2.5), (2.6). Here the algebraically optimized directional separation ranks R_ℓ , $\ell = 1, 2, 3$, are only determined by the entanglement properties of a molecule, while the numbers $N_b^2 - R_\ell$ indicate the measure of redundancy in the product basis set. Normally, we have $R_\ell \ll n$ and $R_\ell \leq N_b$, $\ell = 1, 2, 3$. The asymptotic bound $R_\ell \leq C_\ell |\log \varepsilon| N_{orb}$ is illustrated in Figure 2.1. One can observe that in the case of glycine molecule the first mode-rank is much smaller than others indicating the flattened shape of the molecule.

However, the a priori rank estimate (5.1) looks too pessimistic compared with the results of numerical experiments. However, in the case of flattened or extended molecules (some of directional ranks are small) this estimate provides much lower bound.

The factorization (2.5), (2.6) is a reminiscent of the exact Galerkin representation (2.1), but now in the right RF basis $V^{(\ell)}$, while matrices $M_k^{(\ell)}$ play the role of "directional" Galerkin projections of the Newton kernel onto the left RF basis, $U^{(\ell)}$. This factorization is applied directly to fast calculation of the reduced Cholesky factorization of the matrix B as described in Algorithm 1.

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