Martin Mrovec
Low-rank tensor representation of Slater-type and Hydrogen-like orbitals

Terms of use:

LOW-RANK TENSOR REPRESENTATION OF SLATER-TYPE AND HYDROGEN-LIKE ORBITALS

Martin Mrovec, Ostrava

Abstract. The paper focuses on a low-rank tensor structured representation of Slater-type and Hydrogen-like orbital basis functions that can be used in electronic structure calculations. Standard packages use the Gaussian-type basis functions which allow us to analytically evaluate the necessary integrals. Slater-type and Hydrogen-like orbital functions are physically more appropriate, but they are not analytically integrable. A numerical integration is too expensive when using the standard discretization techniques due the dimensionality of the problem. However, it can be effectively performed using the tensor representation of basis functions. Furthermore, this approach can take advantage of parallel computing.

Keywords: Slater-type orbital; Hydrogen-like orbital; Gaussian-type orbital; electronic structure; tensor numerical methods; sinc approximation

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1. Introduction

In electronic structure computations (Hartree-Fock or Density Functional Theory-based [13]) we encounter calculation of the so-called two electron integrals (TEI) [6]

$$(1.1) \qquad b_{ijkl} = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\varphi_i(\mathbf{x})\varphi_j(\mathbf{x})\varphi_k(\mathbf{y})\varphi_l(\mathbf{y})}{\|\mathbf{x}-\mathbf{y}\|}\, \mathrm{d}^3\mathbf{y}\, \mathrm{d}^3\mathbf{x},$$

where $\varphi_*\colon \mathbb{R}^3 \to \mathbb{R}$ are basis functions, $i,j,k,l \in \{1,2,\ldots,N_B\}$ (N_B is the number of basis functions). This calculation is the main ingredient of the so-called precomputing

phase. In the case of the electronic structure of molecules most of the standard software packages use the Gaussian-type basis (GTO) functions in the form

$$(1.2) \qquad \varphi^{nlm}(x_1, x_2, x_3) = N \cdot x_1^n \cdot x_2^l \cdot x_3^m \cdot \mathrm{e}^{-\alpha(x_1^2 + x_2^2 + x_3^2)}$$

with integer exponents n, l, m, a coefficient $\alpha > 0$ and a normalization constant N. A reason of using such basis is the separability and thus analytical integrability of the TEI. However, GTO basis functions poorly behave in the area of the atomic core, so for the required accuracy of the result of the electronic structure calculation we have to enlarge the number of basis functions. An alternative to GTO functions can be the physically more appropriate Slater-type orbital (STO) functions. Unfortunately in the case of STO functions TEI are not analytically integrable. To overcome this problem the STOs are usually substituted by a linear combination of Gaussians with fixed coefficients. This representation is known as a contracted basis. Coefficients of the linear combination can be obtained in various ways. Several papers present searching of the required coefficients as a solution of the optimization problem [4], [16]. Although this approach leads to finding the best possible approximation (with respect to the chosen norm), the optimization problem is quite complicated and becomes difficult to solve for a higher number of Gaussians. We use a different approach based on the sinc approximation [7]. By using the sinc approximation we can get results which are less accurate (the number of Gaussians required for obtaining an approximation with the given accuracy is higher than in the case of the optimization approach). However, to obtain the linear combination coefficients we only have to evaluate a single-variable function at given points, which is the main advantage of this approach. Furthermore, we know how to make error estimates which describe the dependence of the error on the number of Gaussians.

In the recent paper [5] a concept of numerical integration of TEI (which should be intractable when using direct discretization techniques) based on Tensor numerical methods (TNM) has been described and demonstrated on GTO basis functions. Although by using the Gausian approximation of STO functions the TEI can be evaluated analytically we have chosen the TNM numerical integration. The reason is that we do not want to be limited to work only with Gaussian-based functions. We will follow the TNM scheme here as well so the Gaussian approximation of STO functions will be represented numerically.

This paper follows [12] where the STO basis functions were approximated using the sinc approximation but with a necessity of using algorithms to optimize the so-called canonical rank [5]. Here we present a much more effective approach that utilizes several properties of the Laplace transform and leads to an efficient low-rank approximation directly. Furthermore, the whole concept is simply extended to

Hydrogen-like orbital (HLO) basis functions at similar storage costs. In addition to the physical accuracy, the HLO functions have the partial orthogonality property. It means that HLO functions centered at the same nucleus are orthogonal. This attribute can positively influence the iterative process of the solution of the non-linear eigenvalue problem [13].

The paper is organized as follows. In Section 2 we recapitulate ways how the TNM effectively represent multidimensional data. Next, in Section 3 we recall the sinc approximation method and a way how to use it to find a low rank representation (described in Section 2) of discretized multivariate functions [7]. The main contributions of this paper are introduced in Section 4. We introduce formulas (4.9) and (4.29) that are suitable for using the sinc approximation and which lead to approximation of STO and HLO functions. These formulas are derived using Theorem 4.2, which is also proved here. Furthermore, we derive error estimates of the approximation. In Section 5 results of numerical tests, which validate the correctness of derived formulas, are presented. Finally, concluding remarks are given in Section 6.

2. Low-rank tensor representation of multidimensional data

Recently, several papers aimed at the tensor representation of multidimensional data have been published (e.g. [6], [7], [5]). Nevertheless, for better readability we will mention again the main concepts of the Tensor Numerical Methods. First, let us start with the definition of a tensor.

Definition 2.1. Let $n_1, n_2, \ldots, n_d \in \mathbb{N}$, $d \in \mathbb{N}$. A tensor of order d (N-d tensor) is defined as a multidimensional array over a d-tuple index set, i.e.,

$$(2.1) \qquad \mathbf{A} \in \mathbb{R}^{n_1 \times n_2 \times \ldots \times n_d}, \quad [\mathbf{A}]_{i_1 i_2 \ldots i_d} = a_{i_1 i_2 \ldots i_d} \in \mathbb{R}.$$

Assuming $n_1 = n_2 = \ldots = n_d = n$, we need n^d numbers for storing such tensor in a memory. It is obvious that even for small values of d we quickly lose the ability to store the data in a memory. This phenomenon is known as "Curse of dimensionality". TNM come with special data representations that overcome this problem.

Definition 2.2. Given a tensor $\mathbf{A} \in \mathbb{R}^{n_1 \times \ldots \times n_d}$; a canonical rank of $\mathbf{A}$ is defined as the lowest number R for which there exists a representation

$$(2.2) \qquad \mathbf{A} = \sum_{k=1}^{R} c_k \mathbf{u}_k^{(1)} \otimes \ldots \otimes \mathbf{u}_k^{(d)},$$

where c_k is an expansion coefficient, $\mathbf{u}_k^{(l)} \in \mathbb{R}^{n_l}$ is lth mode vector, $\otimes$ denotes the tensor product. A representation given by formula (2.2) is called the canonical representation.

R e m a r k 2.1.   We can observe that for R the following inequality holds:

$$
(2.3) \qquad 1 \leqslant R \leqslant \min_{l \in \{1, \ldots, d\}} n_l^{-1} \prod_{i=1}^{d} n_i.
$$

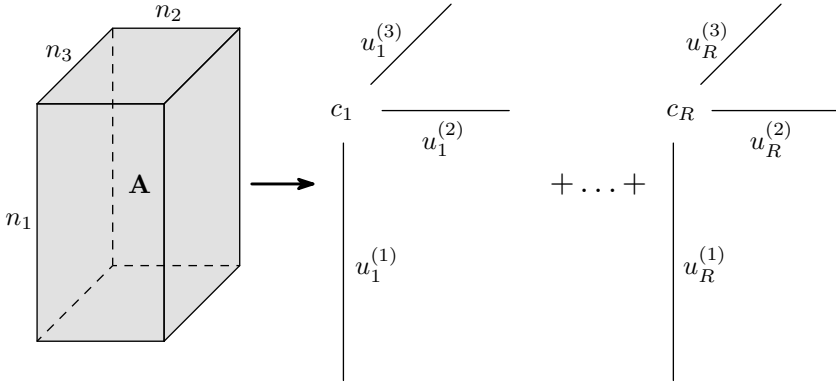An idea of the canonical representation is illustrated on Figure 1.

Figure 1. Canonical representation of a given tensor $\mathbf{A}$.

From now on, we will assume $n_1 = n_2 = \ldots = n_d = n$ for the sake of simplicity. Memory demands of the canonical representation are equivalent to $d \cdot R \cdot n$ numbers. We can see that in the case of a sufficiently low R the memory requirements are much lower than for a full sized tensor. Owing to the inequality given by formula (2.3), this condition may not always be fulfilled. However, we often encounter canonical representations (with normalized mode vectors) where several expansion coefficients are significantly lower than the others, so they can be omitted and consequently the canonical rank is reduced. Of course, in this way, we make an error corresponding to the order of the omitted coefficients.

Besides the low storage costs of the canonical representation we can efficiently perform multilinear algebra operations, such as Hadamard product, dot product and a discrete convolution. Given two tensors with canonical ranks R_1, R_2, the Euclidean dot product, or the Hadamard (entrywise) product takes $d \cdot R_1 \cdot R_2 \cdot n$ operations, the discrete convolution takes $d \cdot R_1 \cdot R_2 \cdot n \cdot \log n$ operations (instead of n^d and $n^3 \cdot \log^3 n$ respectively) [6]. The efficiency of these operations is, among other, important for numerical evaluation of TEI [5]. For purposes of this paper we mention a way how to evaluate the Hadamard product.

Theorem 2.1 (Hadamard product for canonically represented tensors [6])**.** *Given two canonically represented tensors* $\mathbf{A}, \mathbf{B}$ *of the same size,*

$$(2.4) \qquad \mathbf{A} = \sum_{k=1}^{R_A} c_k \mathbf{u}_k^{(1)} \otimes \ldots \otimes \mathbf{u}_k^{(d)},$$

$$(2.5) \qquad \mathbf{B} = \sum_{j=1}^{R_B} d_j \mathbf{v}_j^{(1)} \otimes \ldots \otimes \mathbf{v}_j^{(d)},$$

the Hadamard (entrywise) product can be calculated as

$$(2.6) \qquad \mathbf{A} \odot \mathbf{B} = \sum_{k=1}^{R_A} \sum_{j=1}^{R_B} c_k d_j \bigotimes_{l=1}^{d} (\mathbf{u}_k^{(l)} \odot \mathbf{v}_j^{(l)}).$$

R e m a r k 2.2. Equation 2.6 follows simply from the distributivity of the multiplication operation.

One of the problems related to the canonical representation is that there are no algorithms known to determine the canonical rank of a given full sized tensor. The same holds for searching the best rank R canonical approximation of a given full sized tensor (e.g. with respect to the Frobenius norm). However, in special cases, which include function-related tensors, algorithms for finding satisfactory low-rank approximations are known [7]. One of such methods will be described in the following section.

3. Sinc approximation

The sinc approximation method is a method for finding a separable canonical approximation of multidimensional tensors obtained by an equidistant discretization of multivariate functions on multidimensional intervals [7]. The class of functions, where the method can be used, consists of multivariate functions that are generated by some univariate function u, where its single variable r is substituted by a function of the spatial variables. The principle of the method is based on the fact that some univariate functions can be represented by an integral transformation. A substitution of r by a function of the spatial variables can lead to a separable approximation. Consider a function of one variable $u \colon \mathbb{R} \to \mathbb{R}$ which is given by the integral

$$(3.1) \qquad u(r) = \int_{\Omega} G(t) \cdot e^{F(t) \cdot r^{\gamma}} \, dt$$

with

$$\Omega \in \{\mathbb{R}, \mathbb{R}^+, I\}, \tag{3.2}$$

where I is a closed real interval, $G, F\colon \mathbb{R} \to \mathbb{R}$, and $\gamma \in \mathbb{N}$. This integral can be approximated using a numerical quadrature

$$u(r) \approx \sum_{j=1}^{R} w_j G(t_j) e^{F(t_j)r^\gamma}, \tag{3.3}$$

where t_j are quadrature points and w_j are the corresponding quadrature weights. Function u can generate some multivariate function as mentioned above. Considering r as a function of d variables, e.g.,

$$r = \sum_{l=1}^{d} x_l \tag{3.4}$$

or

$$r = \sqrt{\sum_{l=1}^{d} x_l^2} = \|\mathbf{x}\|, \quad \mathbf{x} \in \mathbb{R}^d, \tag{3.5}$$

we can obtain a separable representation. In the following text we will focus only on the case (3.5) and $\gamma = 2$, i.e.,

$$u(\|\mathbf{x}\|) = \int_\Omega G(t) \cdot e^{F(t) \cdot \|\mathbf{x}\|^2} \, dt \approx \sum_{j=1}^{R} w_j G(t_j) e^{F(t_j)\|\mathbf{x}\|^2}. \tag{3.6}$$

In such a form u can represent radial parts of basis functions which are described in Section 4 (formulas (4.1) and (4.24)). The last term of (3.6) can be rewritten as

$$\sum_{j=1}^{R} w_j G(t_j) \prod_{l=1}^{d} e^{F(t_j)x_l^2}, \tag{3.7}$$

where the spatial variables are separated. Now, we can discretize the function u on a d-dimensional interval. It means that u is represented by a tensor $\mathbf{U} \in \mathbb{R}^{n_1 \times \ldots \times n_d}$ of the order d, where n_l is the number of the equidistant grid points in the lth spatial dimension. Let $\mathbf{y}^l \in \mathbb{R}^{n_l}$ denote a vector of grid points in the lth spatial dimension. Then we can write the canonical representation of $\mathbf{U}$ as

$$\mathbf{U} = \sum_{j=1}^{R} c_j \mathbf{u}_j^{(1)} \otimes \ldots \otimes \mathbf{u}_j^{(d)}, \tag{3.8}$$

where

$$c_j = w_j G(t_j) \tag{3.9}$$

and

$$\mathbf{u}_j^{(l)} = \mathrm{e}^{F(t_j)(\mathbf{y}^{(l)})^2} \tag{3.10}$$

(the second power of $\mathbf{y}^l$ is understood as element-wise).

The remaining question is which type of quadrature should be used to obtain both a satisfying approximation with the low-rank parameter R and a possibility of estimating the approximation error dependence on R. One of such quadratures is the sinc-quadrature [7] based on the interpolation by the sinc function

$$S_{j,h}(t) = \frac{\sin(\pi(t - jh)/h)}{\pi(t - jh)/h}, \quad j \in \mathbb{Z}, \ h \in \mathbb{R}^+. \tag{3.11}$$

Given a one dimensional function $f \colon \mathbb{R} \to \mathbb{R}$ a sinc interpolant is defined as

$$C_{f,h}(t) = \sum_{j=-\infty}^{\infty} f(jh)S_{j,h}(t). \tag{3.12}$$

A sinc interpolant need not necessarily represent the function f exactly (though in some cases it is true [3]). There exist some classes of functions for which $C_{f,h}$ provides a very good approximation [15]. One such space of functions is given by Definition 3.1.

Definition 3.1. Let $\delta \in (0, \frac{1}{2}\pi)$ and

$$D_\delta = \{z \in \mathbb{C} \colon -\delta < \operatorname{Im} z < \delta\}. \tag{3.13}$$

The Hardy space $\mathbb{H}^1(D_\delta)$ is defined as the set of complex functions v that are holomorphic on D_δ and

$$\int_{-\infty}^{\infty} |v(x + \mathrm{i}\delta)| + |v(x - \mathrm{i}\delta)| \, \mathrm{d}x < \infty. \tag{3.14}$$

R e m a r k 3.1. If we write that a real function f belongs to the Hardy space $\mathbb{H}^1(D_\delta)$, then we understand that it is a restriction of a complex function $v \in \mathbb{H}^1(D_\delta)$ to $\mathbb{R}$.

For functions which belong to $\mathbb{H}^1(D_\delta)$ we can approximate their integral over $\mathbb{R}$ using a sinc interpolant:

$$(3.15) \qquad \int_{\mathbb{R}} f(t)\,\mathrm{d}t \approx \int_{\mathbb{R}} C_{f,h}(t)\,\mathrm{d}t = h \cdot \sum_{j=-\infty}^{\infty} f(jh).$$

R e m a r k 3.2. The proof of the last equality in (3.15) can be found for example in [15], Theorem 1.10.1.

In practice we are not able to handle an infinite number of quadrature points so the sum has to be truncated, i.e.

$$(3.16) \qquad \sum_{j=-\infty}^{\infty} f(jh) \approx \sum_{j=-M}^{M} f(jh), \quad M \in \mathbb{N}.$$

For functions which belong to $\mathbb{H}^1(D_\delta)$ and which converge to 0 fast enough as x tends to infinity the error dependence on the canonical rank can be estimated using Theorem 3.1 [15].

Theorem 3.1 (Error of the sinc quadrature). *Let $f \in \mathbb{H}^1(D_\delta)$. If f satisfies*

$$(3.17) \qquad |f(x)| \leqslant C\mathrm{e}^{-b|x|} \quad \forall\, x \in \mathbb{R} \text{ with } C > 0,\ b > 0,$$

then there exists a constant C_1 depending on f, δ and α such that

$$(3.18) \qquad \left| \int_{\mathbb{R}} f(x)\,\mathrm{d}x - h \sum_{j=-M}^{M} f(jh) \right| \leqslant C_1 \mathrm{e}^{-\sqrt{2\pi\delta b M}}$$

with

$$(3.19) \qquad h = \sqrt{\frac{2\pi\delta}{bM}}.$$

Assuming we know the right integral representation (3.6) for the desired multivariate function, we have got all the necessary tools to find its canonical approximation. In the next section we will discuss such representations that lead to a canonical approximation of STO or HLO functions.

4. Approximation of basis functions

In this section we will have a look at integral formulas that will be used to make a canonical approximation of the STO and HLO functions. We will focus on verifying that the formulas are suitable for using the sinc-quadrature and also on estimating the error of the approximation.

4.1. Canonical approximation of the Slater type functions. The STO functions can be written as

$$(4.1) \qquad \varphi^{nlm}(\mathbf{x}) = N \cdot \|\mathbf{x}\|^{n-l-1} \cdot \widetilde{Y}_{lm}(\mathbf{x}) \cdot e^{-\alpha\|\mathbf{x}\|},$$

where N is a normalization constant, $n \in \mathbb{N}$, $l \in \{0, \ldots, n\}$, $m \in \{-l, \ldots, l\}$, and $\widetilde{Y}_{lm}$ denotes a real spherical harmonic [2] multiplied by $\|\mathbf{x}\|^l$, i.e.,

$$(4.2) \qquad \widetilde{Y}_{lm}(\mathbf{x}) = C_{lm} \cdot Q_{lm}(\mathbf{x})$$

with a normalization constant C_{lm} and a multivariate polynomial Q_{lm}. Formula (4.1) can be divided into two parts. The angular part consists of the function $\widetilde{Y}_{lm}(\mathbf{x})$ and the rest is called the radial part. A canonical representation of each part has to be found separately. Let us denote by R_{a} and R_{r} the canonical rank of the discretized angular and of the discretized radial part, respectively. Then the canonical approximation of the whole STO function can be obtained by using formula (2.6). (**A** contains a canonical representation of the discretized radial part and **B** contains a canonical representation of the discretized angular part.) The resulting canonical rank is equal to $R_{\mathrm{a}} \cdot R_{\mathrm{r}}$.

4.1.1. Angular part. The separable canonical representation of the angular part $\widetilde{Y}_{lm}$ is straightforward. If we look at the table of spherical harmonics [2], we can observe that their canonical rank does not exceed 6 for $l \leqslant 4$. For example for $l = 3$, $m = -1$:

$$(4.3) \qquad \widetilde{Y}_{3,-1}(x_1, x_2, x_3) = \frac{1}{4}\sqrt{\frac{21}{2\pi}} \cdot (4x_2 \cdot x_3^2 - x_1^2 \cdot x_2 - x_2^3).$$

Similarly to the discretization of (3.7) we can represent an interval in each spatial dimension by a vector. Then each term of the polynomial on the r.h.s. of (4.3) represents a rank-1 update of the canonical representation (2.2) with rank $R = 3$.

4.1.2. Radial part. Finding a canonical representation of the radial part is not as straightforward as in the case of the angular part. We have to use the sinc approximation method mentioned in Section 3. Using the inverse Laplace transform [14]

(viewing $\|\mathbf{x}\|$ as a one-dimensional variable) we can find that

$$(4.4) \qquad \mathrm{e}^{-\alpha\|\mathbf{x}\|} = \frac{\alpha}{2\sqrt{\pi}} \int_0^\infty t^{-3/2} \cdot \mathrm{e}^{-\alpha^2/4t} \cdot \mathrm{e}^{-t\|\mathbf{x}\|^2} \, \mathrm{d}t,$$

which corresponds to the first equality of equation (3.6). The approach presented in [12] separately uses an approximative canonical representation of (4.4) and an approximative canonical representation of $\|\mathbf{x}\|^\beta$, $\beta \in \mathbb{N} \cup \{0\}$. Canonical rank of such representation depends on canonical ranks of individual parts. For example, if the canonical rank of each part is equal to 20, the resulting canonical representation of the radial part has rank equal to 400 which is quite high for numerical treatment and has to be reduced using special algorithms [10]. However, this complication can be bypassed with one of the Laplace transform properties, which is described by Theorem 4.1 [14].

Theorem 4.1 (Derivative of the Laplace transform with respect to the second variable). *Let $f\colon (0,\infty)^2 \to \mathbb{R}$ be the real function of two variables. Let $f(t,x)$ satisfy conditions for the existence of the Laplace transform (with respect to variable t). Let $F\colon \mathbb{C} \times (0,\infty) \to \mathbb{C}$ be the Laplace transform of f, i.e.*

$$(4.5) \qquad F(s,x) = \mathcal{L}[f(t,x)](s) = \int_0^\infty f(t,x)\mathrm{e}^{-st} \, \mathrm{d}t.$$

Assume that there exists a Laplace transform of the partial derivative of f with respect to x. Then

$$(4.6) \qquad \mathcal{L}\left[\frac{\partial f(t,x)}{\partial x}\right](s) = \frac{\partial F(s,x)}{\partial x}.$$

R e m a r k 4.1. To prove this theorem we can use the Leibniz integral rule supplemented by conditions for infinite domains (see [11], p. 338).

Consider α as the variable x of Theorem 4.1. Then, by repeated application of (4.6) on r.h.s. of (4.4) we obtain

$$(4.7) \qquad \|\mathbf{x}\|^\beta \cdot \mathrm{e}^{-\alpha\|\mathbf{x}\|} = (-1)^\beta \cdot \frac{\partial^\beta}{\partial\alpha^\beta} \mathrm{e}^{-\alpha\|\mathbf{x}\|}$$

$$= (-1)^\beta \int_0^\infty \frac{\partial^\beta}{\partial\alpha^\beta}\left[\frac{\alpha}{2\sqrt{\pi}} \cdot t^{-3/2} \cdot \mathrm{e}^{-\alpha^2/4t}\right] \cdot \mathrm{e}^{-t\|\mathbf{x}\|^2} \, \mathrm{d}t.$$

The derivative inside the integral can be evaluated analytically for an arbitrary n. This formula is quite simple but in this form it is not suitable for applying the

sinc-quadrature. As discussed in [12], the problem can be solved by introducing an appropriate substitution,

$$t = \frac{\alpha^2}{2} e^u,$$ (4.8)

which leads to the formula

$$\|\mathbf{x}\|^\beta \cdot e^{-\alpha\|\mathbf{x}\|} = \int_{-\infty}^{\infty} \frac{1}{\alpha^\beta \sqrt{2\pi}} P_\beta(e^u) \cdot e^{-\frac{1}{2}((2\beta+1)u + e^{-u})} \cdot e^{-\frac{1}{2}e^u \alpha^2 \|\mathbf{x}\|^2} \, du,$$ (4.9)

where P_β is a polynomial. The resulting equation corresponds to the first equality of equation (3.6) and, in addition, enables us to apply the sinc quadrature. Theoretically we can derive P_β for an arbitrary β. However, practically only first few polynomials are needed for generating STO functions used as a basis in electronic structure calculations. First seven polynomials are listed in Table 1.

β	$P_\beta(t)$
0	1
1	$-t + 1$
2	$-3t + 1$
3	$3t^2 - 6t + 1$
4	$15t^2 - 10t + 1$
5	$-15t^3 + 45t^2 - 15t + 1$
6	$-105t^3 + 105t^2 - 21t + 1$

Table 1. First 7 polynomials occurring in the integral formula for approximating the radial part of a STO function.

To show that this form is suitable for using the sinc quadrature we will prove the following theorem.

Theorem 4.2. *Let $\alpha > 0$, $r \geqslant 0$ and let the function $v \colon \mathbb{C} \to \mathbb{C}$ be defined as*

$$v(z) = e^{-\frac{1}{2}(kz + e^{-z})} \cdot e^{-\frac{1}{2}\alpha^2 e^z r}.$$ (4.10)

Then v belongs to Hardy space $\mathbb{H}^1(D_\delta)$, $\delta = \frac{1}{3}\pi$, for each $k \in \mathbb{N}$.

P r o o f. Obviously, v is holomorphic on $\mathbb{C}$ (for an arbitrary $k \in \mathbb{N}$). Hence, it is holomorphic on D_δ for an arbitrary $\delta \in (0, \frac{1}{2}\pi)$. We have to show that v satisfies condition (3.14). Let us write down $v(x + i\delta)$ and its absolute value:

$$v(x + i\delta) = e^{-\frac{1}{2}(kx + ki\delta + e^{-(x+i\delta)} + \alpha^2 e^{x+i\delta} r)},$$ (4.11)

$$|v(x + i\delta)| = e^{-\frac{1}{2}(kx + e^{-x}\cos\delta + \alpha^2 r e^x \cos\delta)}.$$ (4.12)

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We can notice that for an arbitrary $x \in \mathbb{R}$ the maximum of v as a function of r is realized at $r = 0$ so we can estimate an upper bound

(4.13)
$$|v(x + \mathrm{i}\delta)| \leqslant \mathrm{e}^{-\frac{1}{2}(kx + \mathrm{e}^{-x} \cos \delta)}.$$

Analogously, we can write

(4.14)
$$|v(x - \mathrm{i}\delta)| \leqslant \mathrm{e}^{-\frac{1}{2}(kx + \mathrm{e}^{-x} \cos \delta)}.$$

Let us choose $\delta = \frac{1}{3}\pi$. Then we can write

$$\int_{-\infty}^{\infty} \left|v\left(x + \mathrm{i}\frac{\pi}{3}\right)\right| + \left|v\left(x - \mathrm{i}\frac{\pi}{3}\right)\right| \mathrm{d}x \leqslant \int_{-\infty}^{\infty} 2\mathrm{e}^{-\frac{1}{2}(kx + \frac{1}{2}\mathrm{e}^{-x})} \mathrm{d}x$$

$$= \left| \begin{array}{c} \text{subst.} \\ \mathrm{e}^{-x} = a \\ -\mathrm{e}^{-x}\,\mathrm{d}x = \mathrm{d}a \end{array} \right| = 2 \int_0^{\infty} a^{\frac{1}{2}k-1} \cdot \mathrm{e}^{-\frac{1}{4}a} \,\mathrm{d}a = 2Y\left(\frac{1}{4}\right),$$

where $Y(s) = \mathcal{L}\big[a^{\frac{1}{2}k-1}\big](s)$ with respect to variable a. Using the Laplace transform table [14], we can find that

(4.15)
$$Y(s) = s^{2/k}\Gamma\left(\frac{k}{2}\right).$$

Finally, we can write

(4.16)
$$2Y\left(\frac{1}{4}\right) = 2^{k+1}\Gamma\left(\frac{k}{2}\right) < \infty,$$

so $v \in \mathbb{H}^1(D_{\pi/3})$ for an arbitrary $k \in \mathbb{N}$. $\qquad \square$

Theorem 4.2 implies that the integrand of the right-hand side of (4.9) belongs to the Hardy space $\mathbb{H}^1(D_{\pi/3})$. Now we can derive an error estimate using Theorem 3.1, which means that we have to find $C > 0, b > 0$ such that

(4.17)
$$\frac{\zeta_\kappa}{\alpha^\beta \sqrt{2\pi}}\mathrm{e}^{-\frac{1}{2}(kx + \mathrm{e}^{-x})} \leqslant C\mathrm{e}^{-b|x|} \quad \forall x \in \mathbb{R},$$

where ζ_κ is one of the expansion coefficients of the polynomial P_β, i.e.,

(4.18)
$$P_\beta(x) = \sum_{\kappa=0}^{\deg P_\beta} \zeta_\kappa x^\kappa.$$

The inequality (4.17) can be rewritten to

(4.19)
$$\frac{\zeta_\kappa}{\alpha^\beta \sqrt{2\pi}}\mathrm{e}^{-\frac{1}{2}kx - \frac{1}{2}\mathrm{e}^{-x} + b|x|} \leqslant C \quad \forall x \in \mathbb{R}.$$

We can notice, that the left-hand side is bounded if $0 < b \leqslant \frac{1}{2}k$. We would like to have an error estimate with the greatest possible b to get the fastest error decrease, so we choose $b = \frac{1}{2}k$. By analysis of the maxima of the l.h.s. of (4.19) we get

$$(4.20) \qquad C = \begin{cases} \dfrac{\zeta_\kappa}{\alpha^\beta \sqrt{2\pi}} & \text{if } k = 1, \\[2ex] \dfrac{\zeta_\kappa}{\alpha^\beta \sqrt{2\pi}} \cdot \left(\dfrac{2k}{\mathrm{e}}\right)^k & \text{if } k > 1. \end{cases}$$

We have to take the lowest possible k generated by β in the product

$$P_\beta(\mathrm{e}^u) \cdot \mathrm{e}^{-\frac{1}{2}((2\beta+1)u + \mathrm{e}^{-u})}$$

as shown in Example 4.1.

E x a m p l e 4.1.   Assume $\beta = 2$. Then we can write

$$P_2(\mathrm{e}^u) \cdot \mathrm{e}^{-\frac{1}{2}(5u + \mathrm{e}^{-u})} = \mathrm{e}^{-\frac{1}{2}(\mathbf{5}u + \mathrm{e}^{-u})} - 3\mathrm{e}^{-\frac{1}{2}(\mathbf{3}u + \mathrm{e}^{-u})},$$

which implies $k = 3$.

All the assumptions of Theorem 3.1 are fulfilled so we can write the error estimate

$$(4.21) \qquad \left| \|\mathbf{x}\|^\beta \cdot \mathrm{e}^{-\alpha\|\mathbf{x}\|} - h \cdot \sum_{j=-M}^{M} I(jh, \|\mathbf{x}\|) \right| \leqslant C_1 \mathrm{e}^{-\sqrt{\pi^2 kM/3}},$$

where $C_1 > 0$,

$$(4.22) \qquad I(u, \|\mathbf{x}\|) = \frac{1}{\alpha^\beta \sqrt{2\pi}} P_\beta(\mathrm{e}^u) \cdot \mathrm{e}^{-\frac{1}{2}((2\beta+1)u + \mathrm{e}^{-u})} \cdot \mathrm{e}^{-\frac{1}{2}\mathrm{e}^u \alpha^2 \|\mathbf{x}\|^2}$$

and

$$(4.23) \qquad h = \sqrt{\frac{4\pi^2}{3kM}}.$$

The error estimate will be validated in the numerical experiments section.

4.2. Canonical approximation of the Hydrogen-like orbital functions.
The HLO functions can be written as

$$(4.24) \qquad \varphi^{nlm}(\mathbf{x}) = N \cdot L_{n-l-1}^{2l+1}\left(\frac{\alpha}{n}\|\mathbf{x}\|\right) \cdot \widetilde{Y}_{lm}(\mathbf{x}) \cdot \mathrm{e}^{-(\alpha/2n)\|\mathbf{x}\|},$$

where N is a normalization constant, $n \in \mathbb{N}$, $l \in \{0, \ldots, n\}$, $m \in \{-l, \ldots, l\}$, $\widetilde{Y}_{lm}$ are the spherical harmonics mentioned in Section 4.1 (equation (4.2)), and L_{n-l-1}^{2l+1} are associated Laguerre polynomials, that can be written as [1]

$$(4.25) \qquad L_{n-l-1}^{2l+1}(x) = \sum_{i=0}^{n-l-1} \mu_i x^i,$$

where

$$(4.26) \qquad \mu_i = \frac{(-1)^i}{i!} \cdot \binom{n+l}{n-l-1-i}.$$

Similarly to STO functions we have to find canonical representations of the radial and the angular parts separately. The angular part is the same as in the case of STO functions, so in this subsection we will concentrate only on the radial part. We have to find a low-rank canonical approximation of

$$(4.27) \qquad R_{nl}(\|\mathbf{x}\|) := L_{n-l-1}^{2l+1}\left(\frac{\alpha}{n}\|\mathbf{x}\|\right) \cdot e^{-(\alpha/2n)\|\mathbf{x}\|}.$$

Here we can use formula (4.9) derived in Section 4.1. Moreover, we exploit a linearity property of the Laplace transform, which is summarized in Theorem 4.3 [14].

Theorem 4.3 (Linearity of the Laplace transform). *Let f_1, f_2 be real functions which satisfy conditions for the existence of the Laplace transform and let F_1, F_2 be their Laplace transforms. Then for any $a_1, a_2 \in \mathbb{R}$*

$$(4.28) \qquad \mathcal{L}[a_1 f_1(t) + a_2 f_2(t)](s) = a_1 F_1(s) + a_2 F_2(s).$$

By combining equations (4.9), (4.25), (4.26), (4.27), and (4.28), we obtain the final radial part integral representation formula

$$(4.29)\quad R_{nl}(\|\mathbf{x}\|) = \int_{-\infty}^{\infty} \sum_{i=0}^{n-l-1} \left[\frac{\mu_i 2^i}{\sqrt{2\pi}} \cdot P_i(e^u) \cdot e^{-\frac{1}{2}((2i+1)u + e^{-u})} \right] \cdot e^{-(1/8n^2)e^u \alpha^2 \|\mathbf{x}\|^2} \, du,$$

which is suitable for applying the sinc quadrature (as follows from Theorem 4.2). Due to the similarity to formula (4.9) we can expect the exponential error decrease with respect to the canonical rank.

5. NUMERICAL EXPERIMENTS

The aim of this section is to verify the estimates made in Section 4 for the radial parts of STO and HLO functions. Further, a possibility of a cheap rank reduction will be discussed.

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5.1. Approximation of STO functions. Figure 2 contains graphs of the radial parts of the first four STO functions with $\alpha = 1$.
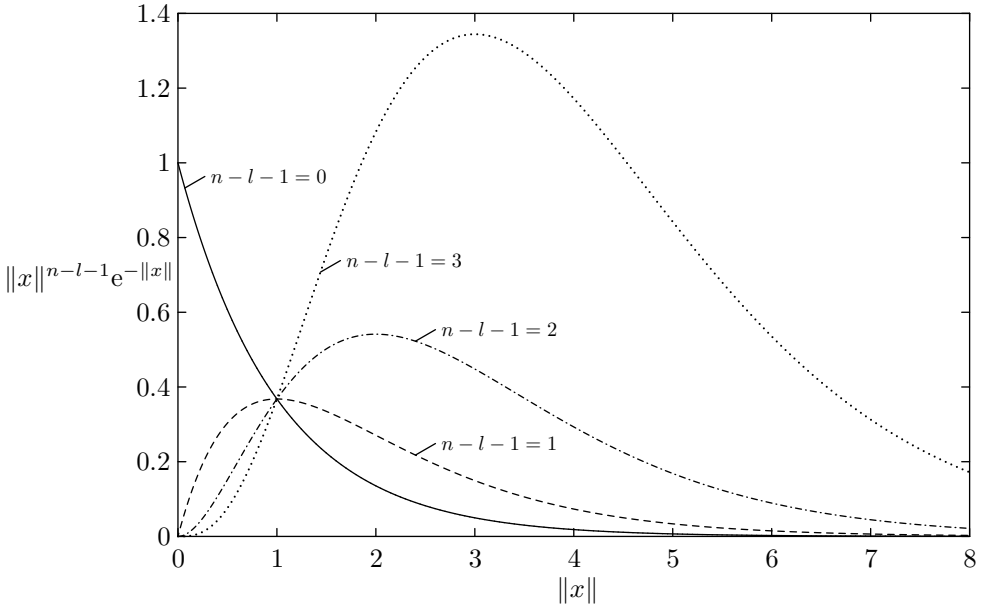

Figure 2. Radial parts of the first four STO functions with $n - l - 1$ as an exponent of $\|\mathbf{x}\|$.

For these functions the error estimate (4.21) was tested. The absolute error is measured as the maximum of the absolute value of the difference between the analytical formula of the STO radial part (equation (4.1) without $\widetilde{Y}_{lm}(\mathbf{x})$) and the approximation given by equation (4.9) with the applied sinc quadrature. For error measurements both functions are equidistantly discretized on a finite interval. The sinc-quadrature step h is determined by formula (4.23). For the first two functions the parameter k was set to 1, and for the other functions k was set to 3. This setting is determined by the degree of the polynomial P_β. Figures 3 and 4 show the dependence of the absolute error on the canonical rank.

Both figures confirm that the error estimate is correct.

5.2. Approximation of HLO functions. Figure 5 contains graphs of the radial parts of the first four HLO functions with $\alpha = 1$.

We can observe that $R_{10}(\|\mathbf{x}\|)$ and $R_{21}(\|\mathbf{x}\|)$ are functions that represent radial parts of STO basis functions so the tests of them had already been performed in the previous subsection and are thus skipped here. Due to the similarity of the integral formulas of HLO and STO radial parts we can use the same error estimate as in the case of the STO function. The sinc-quadrature step h is also determined by
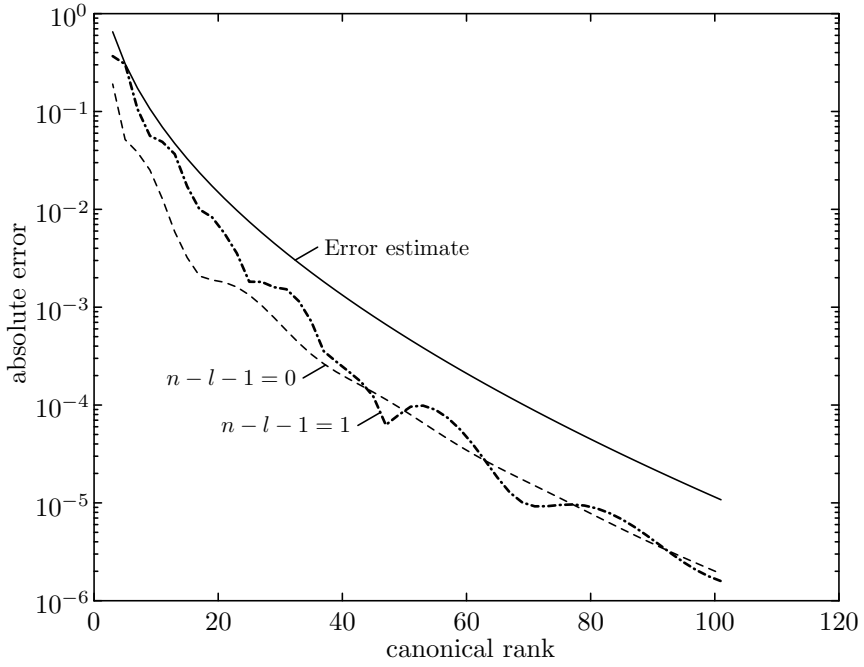
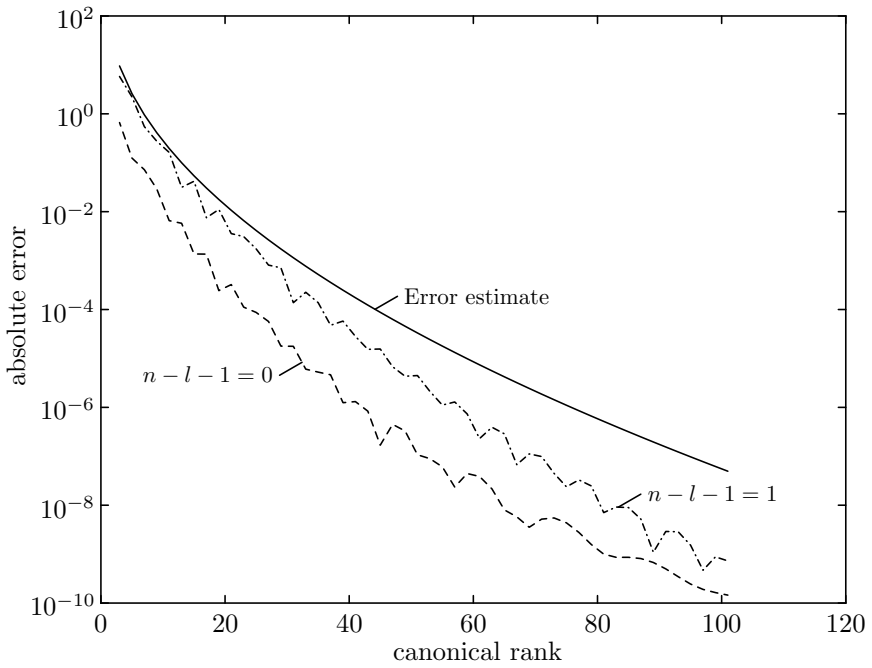Figure 3. Error dependence on rank-radial part of STO with $n - l - 1 \in \{0, 1\}$.

Figure 4. Error dependence on rank-radial part of STO with $n - l - 1 \in \{2, 3\}$.
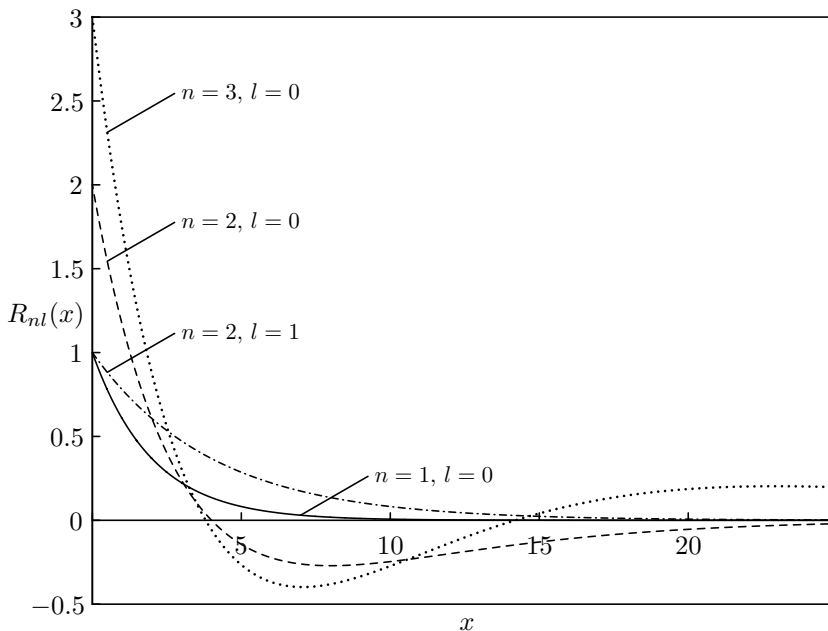
Figure 5. Radial parts of the first four HLO functions.

formula (4.23). The parameter k was set to 1, because the integral formula always contains the polynomial P_0. Figures 6 and 7 show the dependence of the absolute error on the canonical rank.

Both figures confirm that the error estimate is correct.

5.3. Rank reduction. In Section 2 we have mentioned a possibility of a reduction of the canonical rank when the mode vectors of the canonical representation (2.2) are normalized (e.g. with respect to the Euclidean norm). The reduction can be performed by omitting rank-1 contributions, where absolute values of coefficients c_k are lower than some $\varepsilon > 0$. Using the rank reduction, the storage costs of the canonical representation can be significantly reduced. In this subsection we discuss a rank reduction of canonical representations of radial parts of STO and HLO functions obtained by the sinc approximation method. We can notice that mode vectors of the generated canonical representation do not contain numbers with modulus greater than 1. Therefore, by omitting $R_0 \in \mathbb{N}$ rank-1 contributions with $|c_k| < \varepsilon$ the absolute error of the approximation may at maximum increase by $\varepsilon \cdot R_0$. The rank reduction has been tested for all approximations tested above and results were practically the same. As an example, Figure 8 illustrates how the canonical rank can be reduced if we set $\varepsilon = 10^{-15}$ in the case of the radial part of the STO with $n-l-1 = 2$.
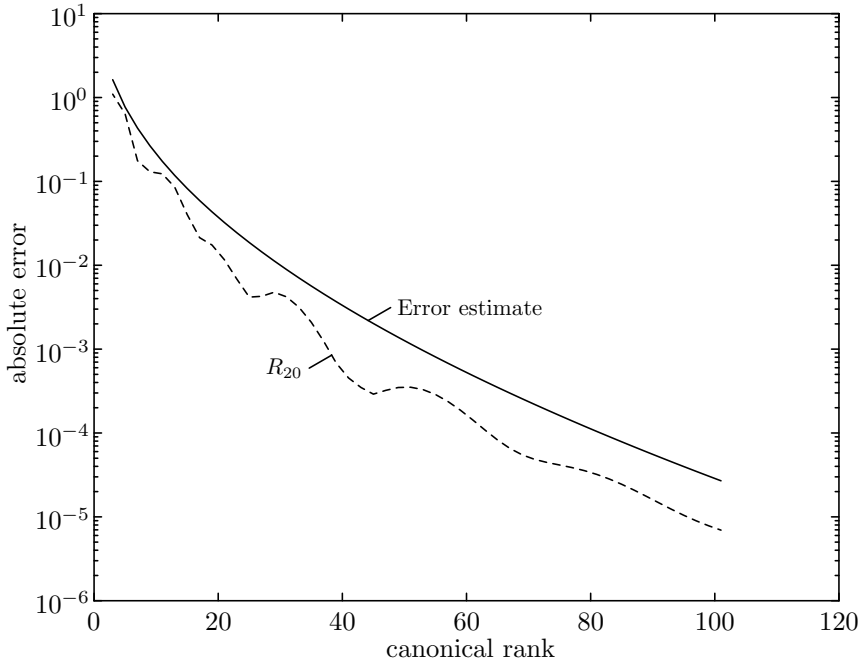
Figure 6. Error dependence on rank-radial part of HLO with $n = 2, l = 0$.
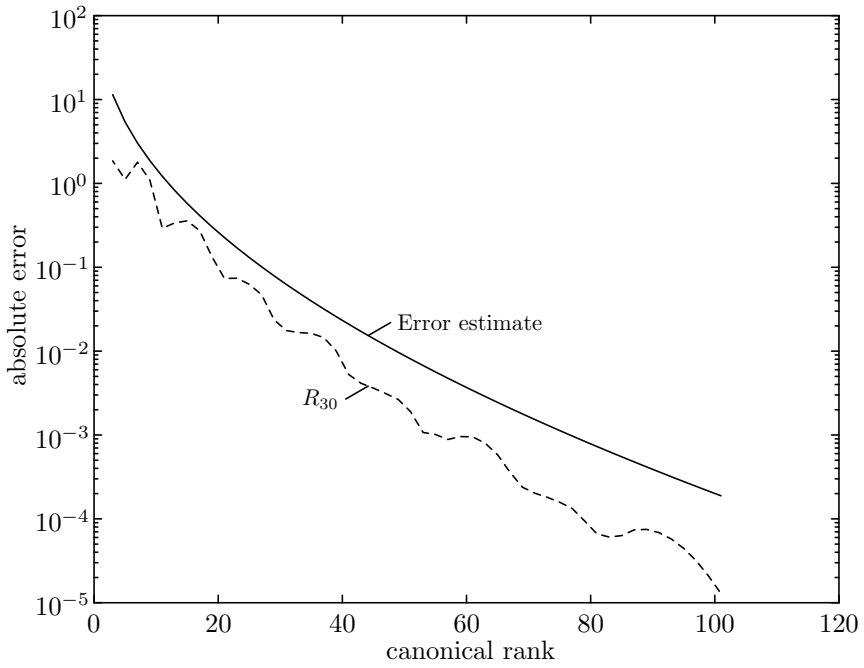

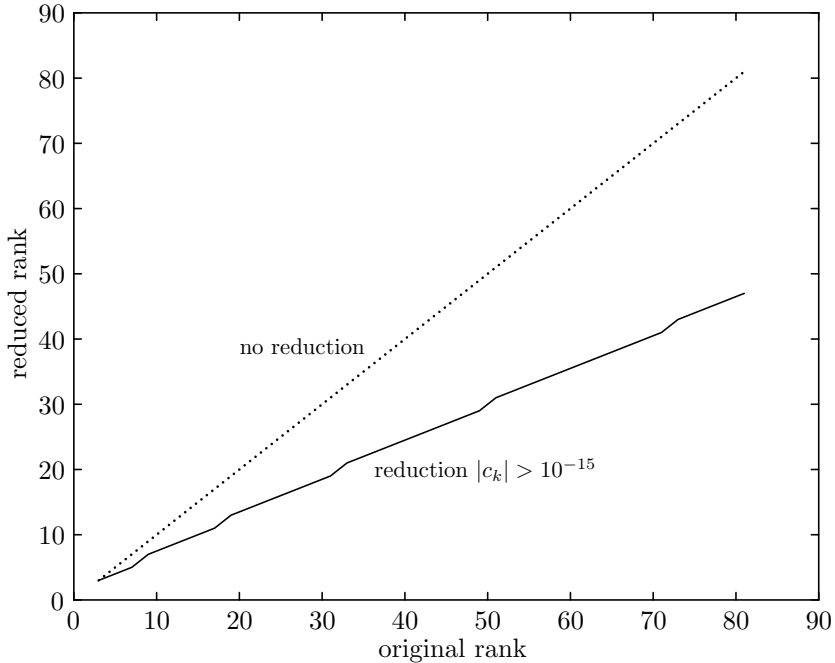Figure 7. Error dependence on rank-radial part of HLO with $n = 3, l = 0$.

Figure 8. Rank reduction by omitting expansion coefficients c_k with modulus lower than 10^{-15}—STO with $n - l - 1 = 2$.

We observe that using the rank reduction the memory costs can be almost halved.

6. CONCLUSION

In this paper we have discussed formulas which lead to a low-rank approximation of multivariate functions, which can be used as bases within the electronic structure calculations. Compared to recent paper [12] a much more efficient way to get a low-rank approximation of the STO function has been presented. For comparison the previous approach generated a canonical tensor with rank $R = 1200$ and with an error of the order of 10^{-2}, whereas using the approach presented in this paper we obtain a tensor with the canonical rank equal to 18 at the same error. Moreover, the rank can be reduced up to 11 by omitting rank-1 contributions with low expansion coefficients. Further, the method has been used for approximation of HLO functions that make up an orthogonal set (assuming that they are centered at the same point in the 3D space). This fact can positively influence the iterative process of the solution of the non-linear eigenvalue problem. Finally, we should note that in addition to the canonical representation there exist other rank-structured tensor formats, e.g. the Tucker format or the TT representation [8]. We should also mention [9], where

a numerical analysis of the low-rank representation of the Slater-type radial function in the Tucker format has been reported.

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Author's address: *Martin Mrovec*, Department of Applied Mathematics & IT4Innovations—National Supercomputing Center, VŠB—Technical University of Ostrava, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic, e-mail: `martin.mrovec@vsb.cz`.