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single-electron systems

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Abstract

Tensor product (TP) approximation with optimal tensor rank provides an interesting alternative to the traditional Gaussian-type orbital (GTO) basis functions in electronic structure calculations. The GTO basis functions are commonly used in electronic structure calculations for approximation of single-electron wavefunctions the so-called orbitals. The rigorous results are available only for the H atom concerning the approximation errors of GTO bases for the solution of the single-electron Schrödinger equation. In this paper, we apply the TP approximation to the H atom for computation of the kinetic energy and potential energy. We then apply the TP approximation to the single-electron systems with several nuclei and study the accuracy of the approximation. We also study the sparse wavelet representation of univariate components of the TP approximation which paves the way for the fast computation of various integrals involving the orbitals and orbital products in electronic structure methods.

This article is dedicated to Prof. Dr. Dr. h.c. Wolfgang Hackbusch
in honour of his sixtieth birthday.

1 Introduction

Tensor product approximations have a long and successful history in quantum chemistry. Beylkin and Mohlenkamp [3, 4] initiated a program for low rank tensor product decompositions in electronic structure calculations. Recently, tensor product approximation [5, 6, 14, 11] has been applied in electronic structure calculations for efficient computation of Coulomb integrals. The basic idea to represent certain quantities in tensor products is to factorize the expensive parts of the calculation in order to reduce the dimensionality and thereby the computational complexity. The prominent example for tensor products in quantum chemistry are GTO basis sets for the approximation of single-electron wavefunctions (orbitals) and related quantities like one-electron orbital product density and total electron density. The GTO basis functions are widely used in electronic structure calculations. There are several advantages

to use Gaussians, for instance the product of two Gaussian functions is again a Gaussian and integral evaluation is much easier. The GTO basis functions achieve almost exponential convergence rates $\sigma_\kappa(\psi_H) \sim e^{-\mu\sqrt{\kappa}}$ for the H atom [15, 1]. We propose an “optimal” TP approximation for electronic structure calculations [5]. The TP approximation with “optimal” tensor rank provides an interesting alternative to the traditional GTO basis functions in quantum chemistry. The “optimal” TP approximation is performed in the sense that for a given accuracy an approximate tensor representation with minimal rank is determined. It is the so-called best tensor rank κ approximation. Using best tensor rank κ approximation and wavelet techniques, we want to construct algorithms for the fast computation of various integrals which appear commonly in electronic structure methods. These integrals are very complicated and involve orbitals, orbital products and electron density. We therefore study the TP approximation of single-electron systems and sparse wavelet representation. This paves us the way for the fast algorithms to compute the complicated integrals in electronic structure methods. For this we first study the TP approximation to the H atom, because the rigorous results are available only for the H atom concerning the approximation errors of GTO bases.

2 The TP approximation for the kinetic energy of the H atom

To obtain the best tensor rank κ approximations to the H atom, we need to obtain the best tensor rank κ approximations of the solution of the single-electron Schrödinger equation

$$\left[-\frac{1}{2}\Delta_{\mathbf{x}} - \sum_{\mathbf{A}} \frac{Z_A}{|\mathbf{x} - \mathbf{R}_A|} \right] \psi^{GTO}(\mathbf{x}) = \varepsilon_0 \psi^{GTO}(\mathbf{x}), \quad (1)$$

for the kinetic energy and also for the potential energy. We study here the error of the best tensor rank κ approximation for the kinetic energy of the H atom. For this, we solve the single-electron Schrödinger equation (1) by using MOLPRO (a standard quantum chemistry package) [18]. To solve the Schrödinger equation, we use an uncontracted GTO basis with exponents taken from a V6Z basis set. The approximate solution of the single-electron Schrödinger equation, i.e., the spatial orbital has the following form

$$\psi^{GTO}(\mathbf{x}) = \sum_{k=1}^K c_k g_k^{(1)}(x_1) g_k^{(2)}(x_2) g_k^{(3)}(x_3), \quad (2)$$

where c_k are the coefficients including normalization constants and K is the initial rank, i.e., the total number of Gaussians used to represent the spatial orbital $\psi^{GTO}(\mathbf{x})$ and

$$g_k^{(i)}(x_i) = e^{-\alpha_k(x_i - A_k^{(i)})^2} \quad \text{for } i = 1, 2, 3. \quad (3)$$

Here $A_k^{(i)}$ for $i = 1, 2, 3$ are the centres of the Gaussians, and α_k are the exponents of the Gaussians. The individual Gaussians in each direction are represented in terms of interpolating scaling functions

$$g_k^{(i)}(x_i) \approx \sum_a b_{k,j,a}^{(i)} \phi_{j,a}(x_i) \quad \text{with } b_{k,j,a}^{(i)} = 2^{-j/2} g_k^{(i)}(2^{-j}a). \quad (4)$$

We use here the interpolating scaling functions $\phi_{j,a}(x) := 2^{j/2}\phi(2^j x - a)$; $j, a \in \mathbb{Z}$ of Deslauriers and Dubuc [9]. It should be mentioned that $j \in \mathbb{Z}$ is the resolution level and $a \in \mathbb{Z}$ is the translation parameter. These interpolating scaling functions are very good to represent the polynomials up to the degree 5. In the next step we obtain the best tensor rank κ approximations of the spatial orbital

$$\psi^{GTO}(\mathbf{x}) \approx \sum_{k=1}^{\kappa} h_k^{(1)}(x_1) h_k^{(2)}(x_2) h_k^{(3)}(x_3) := \psi^{TPA}(\mathbf{x}) \quad (5)$$

$$= \sum_{k=1}^{\kappa} \left(\sum_{a_1} f_{k,a_1}^{(1)} \phi_{j,a_1}(x_1) \right) \left(\sum_{a_2} f_{k,a_2}^{(2)} \phi_{j,a_2}(x_2) \right) \left(\sum_{a_3} f_{k,a_3}^{(3)} \phi_{j,a_3}(x_3) \right), \quad \kappa \ll K. \quad (6)$$

The error of the approximations with fixed rank κ may be defined via

$$\sigma_{\kappa}(\psi^{GTO}) := \inf_{h_k^{(i)} \in l^2(\mathbb{R})} \left\| \psi^{GTO} - \sum_{k=1}^{\kappa} h_k^{(1)} \otimes h_k^{(2)} \otimes h_k^{(3)} \right\|_{l^2(\mathbb{R}^3)} \quad (7)$$

and is minimized with respect to the l^2 -norm. This problem is solved by using variations of the Newton method. More details have already been discussed in our previous article [5] and also in [6]. Once we have got the best tensor rank κ approximations of the spatial orbital, we can obtain the corresponding approximation error for the kinetic energy of the H atom. The kinetic energy operator of the H atom is

$$T_{KE} = -\frac{1}{2} \Delta_{\mathbf{x}}. \quad (8)$$

The expectation value of the kinetic energy for orbital $\psi^{GTO}(\mathbf{x})$ is

$$T = \langle T_{KE} \rangle = -\frac{1}{2} \int_{\mathbb{R}^3} \psi^{GTO}(\mathbf{x}) \Delta_{\mathbf{x}} \psi^{GTO}(\mathbf{x}) d\mathbf{x}. \quad (9)$$

If we substitute the best tensor rank κ approximation of the spatial orbital for the H atom (5) in Eq. (9), we obtain

$$\begin{aligned} T &\approx -\frac{1}{2} \int_{\mathbb{R}^3} \psi^{TPA}(\mathbf{x}) \Delta_{\mathbf{x}} \psi^{TPA}(\mathbf{x}) d\mathbf{x} \\ &= -\frac{1}{2} \sum_{k=1}^{\kappa} \sum_{k'=1}^{\kappa} \left\{ \left[\left(\sum_{a_1} f_{k,a_1}^{(1)} f_{k',a_1}^{(1)} \langle \phi_{j,a_1} | \Delta_1 | \phi_{j,b_1} \rangle \right) \right. \right. \\ &\quad \left. \left(\sum_{a_2} \sum_{b_2} f_{k,a_2}^{(2)} f_{k',b_2}^{(2)} \langle \phi_{j,a_2} | \phi_{j,b_2} \rangle \right) \left(\sum_{a_3} \sum_{b_3} f_{k,a_3}^{(3)} f_{k',b_3}^{(3)} \langle \phi_{j,a_3} | \phi_{j,b_3} \rangle \right) \right] \\ &\quad + \left[\left(\sum_{a_1} \sum_{b_1} f_{k,a_1}^{(1)} f_{k',b_1}^{(1)} \langle \phi_{j,a_1} | \phi_{j,b_1} \rangle \right) \left(\sum_{a_2} \sum_{b_2} f_{k,a_2}^{(2)} f_{k',b_2}^{(2)} \langle \phi_{j,a_2} | \Delta_2 | \phi_{j,b_2} \rangle \right) \right. \\ &\quad \left. \left(\sum_{a_3} \sum_{b_3} f_{k,a_3}^{(3)} f_{k',b_3}^{(3)} \langle \phi_{j,a_3} | \phi_{j,b_3} \rangle \right) \right] \\ &\quad + \left[\left(\sum_{a_1} \sum_{b_1} f_{k,a_1}^{(1)} f_{k',b_1}^{(1)} \langle \phi_{j,a_1} | \phi_{j,b_1} \rangle \right) \left(\sum_{a_2} \sum_{b_2} f_{k,a_2}^{(2)} f_{k',b_2}^{(2)} \langle \phi_{j,a_2} | \phi_{j,b_2} \rangle \right) \right. \\ &\quad \left. \left(\sum_{a_3} \sum_{b_3} f_{k,a_3}^{(3)} f_{k',b_3}^{(3)} \langle \phi_{j,a_3} | \Delta_3 | \phi_{j,b_3} \rangle \right) \right] \left. \right\}. \quad (10) \end{aligned}$$

Eq. (10) is the kinetic energy obtained from the best tensor rank κ approximation of the solution of the single-electron Schrödinger equation. The kinetic energy integrals

$$\langle \phi_{j,a_1} | \Delta_1 | \phi_{j,b_1} \rangle = \int \phi_{j,a_1}(x_1) \Delta_1 \phi_{j,b_1}(x_1) dx_1 \quad (11)$$

and overlap integrals

$$\langle \phi_{j,a_1} | \phi_{j,b_1} \rangle = \int \phi_{j,a_1}(x_1) \phi_{j,b_1}(x_1) dx_1 \quad (12)$$

that appear in Eq. (10) are computed by using an iterative method originally suggested by Beylkin [2], Dahmen and Micchelli [7]. More details for the computation of overlap integrals $\langle \phi_{j,a_1} | \phi_{j,b_1} \rangle$ and kinetic energy integrals $\langle \phi_{j,a_1} | \Delta_1 | \phi_{j,b_1} \rangle$ are given in Appendix A. Fig. 1 shows the error in the kinetic energy for the best tensor rank κ approximation for varying tensor rank κ . As we can see, the error decreases almost exponentially with increasing tensor rank.

3 The TP approximation for the potential energy of the H atom

In this section, we study the TP approximation error for the potential energy of the H atom. The external Coulomb potential seen by an electron in the H atom is

$$T_{PE} = -\frac{1}{|\mathbf{x} - \mathbf{R}_A|}. \quad (13)$$

The expectation value of the potential energy for the orbital $\psi^{GTO}(\mathbf{x})$ is

$$\begin{aligned} V = \langle T_{PE} \rangle &= -\int_{\mathbb{R}^3} \psi^{GTO}(\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{R}_A|} \psi^{GTO}(\mathbf{x}) d\mathbf{x} \\ &= -\int_{\mathbb{R}^3} \frac{\rho^{GTO}(\mathbf{x})}{|\mathbf{x} - \mathbf{R}_A|} d\mathbf{x}, \end{aligned} \quad (14)$$

where

$$\rho^{GTO}(\mathbf{x}) = \psi^{GTO}(\mathbf{x}) \psi^{GTO}(\mathbf{x}) \quad (15)$$

is the so-called one-electron orbital product density. If we use an “approximate resolution of identity”, i.e., a projection onto span $\{\tilde{\beta}_{j,\mathbf{a}} : \mathbf{a} \in \mathbb{Z}^3\}$

$$\mathbb{I} \approx \sum_{\mathbf{a}} |\beta_{j,\mathbf{a}}\rangle \langle \tilde{\beta}_{j,\mathbf{a}}|, \quad (16)$$

then the potential energy can be expressed as

$$\int_{\mathbb{R}^3} \frac{\rho^{GTO}(\mathbf{x})}{|\mathbf{x} - \mathbf{R}_A|} d\mathbf{x} \approx \sum_{\mathbf{a}} \left\langle \frac{1}{|\mathbf{x} - \mathbf{R}_A|} | \beta_{j,\mathbf{a}} \right\rangle \langle \tilde{\beta}_{j,\mathbf{a}} | \rho^{GTO} \rangle, \quad (17)$$

where $\mathbf{R}_A \in 2^{-j} \mathbb{Z}^3$. Here, $\beta_{j,\mathbf{a}}(\mathbf{x}) = \phi_{j,a_1}(x_1) \phi_{j,a_2}(x_2) \phi_{j,a_3}(x_3)$ are isotropic 3d interpolating scaling functions and $\tilde{\beta}_{j,\mathbf{a}}(\mathbf{x})$ are dual scaling functions. The Coulomb potential can be expressed in terms of an integral over a Gaussian function [10]

$$\frac{1}{|\mathbf{x} - \mathbf{R}_A|} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp[-|\mathbf{x} - \mathbf{R}_A|^2 t^2] dt. \quad (18)$$

This representation enables factorization of the following three-dimensional integral of Eq. (17)

$$\begin{aligned} \left\langle \frac{1}{|\mathbf{x} - \mathbf{R}_A|} | \beta_{j,\mathbf{a}} \right\rangle &= \int_{-\infty}^{+\infty} \frac{\phi_{j,a_1}(x_1) \phi_{j,a_2}(x_2) \phi_{j,a_3}(x_3)}{|\mathbf{x} - \mathbf{R}_A|} d\mathbf{x} \\ &= \frac{2}{\sqrt{\pi}} 2^{-j/2} \int_0^\infty \mathcal{I}(t, \mathbf{a}, \mathbf{A}) dt, \end{aligned} \quad (19)$$

where

$$\mathcal{I}(t, \mathbf{a}, \mathbf{A}) = G(t, a_1, A_1) G(t, a_2, A_2) G(t, a_3, A_3) \quad (20)$$

and

$$G(t, a, A) = \int_{-\infty}^{+\infty} \exp[-(x + a - A)^2 t^2] \phi(x) dx. \quad (21)$$

The general procedure to compute integrals (21) is discussed by Flad et al. [10]. We then need an efficient quadrature formula for the integral on the right-hand side of Eq. (19). We therefore use an exponential quadrature formula [17]

$$\int_0^\infty \mathcal{I}(t, \mathbf{a}, \mathbf{A}) dt \approx \tau \sum_{m=-M}^M e^{m\tau} \mathcal{I}(e^{m\tau}, \mathbf{a}, \mathbf{A}), \quad (22)$$

for $\tau = \sqrt{\frac{2\pi\delta}{M}}$ with $\delta < \frac{\pi}{4}$, which provides a uniform error bound with respect to the translation parameter \mathbf{a} . The integration error decreases almost exponentially with respect to the total number of quadrature points $2M + 1$. If we use Eq. (22) and Eq. (19) in Eq. (17), then Eq. (17) becomes

$$\int_{\mathbb{R}^3} \frac{\rho^{GTO}(\mathbf{x})}{|\mathbf{x} - \mathbf{R}_A|} d\mathbf{x} \approx \frac{2\tau}{\sqrt{\pi}} 2^{-j/2} \sum_{\mathbf{a}} \sum_{m=-M}^M e^{m\tau} \mathcal{I}(e^{m\tau}, \mathbf{a}, \mathbf{A}) \langle \tilde{\beta}_{j,\mathbf{a}} | \rho^{GTO} \rangle. \quad (23)$$

We now need the best tensor rank κ approximation of one-electron orbital product density $\rho^{GTO}(\mathbf{x})$. It can be obtained as in the case of the solution of the single-electron Schrödinger equation for the H atom. It is given as

$$\rho^{GTO}(\mathbf{x}) \approx \sum_{k=1}^{\kappa} \varrho_k^{(1)}(x_1) \varrho_k^{(2)}(x_2) \varrho_k^{(3)}(x_3) := \rho^{TPA}(\mathbf{x}), \quad \kappa \ll K(K+1)/2. \quad (24)$$

If we insert the best tensor rank κ approximation of one-electron orbital product density for the H atom (24) in Eq. (23), then

$$\begin{aligned} V &= - \int_{\mathbb{R}^3} \frac{\rho^{GTO}(\mathbf{x})}{|\mathbf{x} - \mathbf{R}_A|} d\mathbf{x} \\ &\approx - \frac{2\tau}{\sqrt{\pi}} 2^{-j/2} \sum_{k=1}^{\kappa} \sum_{m=-M}^M e^{m\tau} \left\{ \left[\sum_{a_1} G(e^{m\tau}, a_1, A_1) \langle \tilde{\phi}_{j,a_1} | \varrho_k^{(1)} \rangle \right] \right. \\ &\quad \left[\sum_{a_2} G(e^{m\tau}, a_2, A_2) \langle \tilde{\phi}_{j,a_2} | \varrho_k^{(2)} \rangle \right] \\ &\quad \left. \left[\sum_{a_3} G(e^{m\tau}, a_3, A_3) \langle \tilde{\phi}_{j,a_3} | \varrho_k^{(3)} \rangle \right] \right\}. \end{aligned} \quad (25)$$

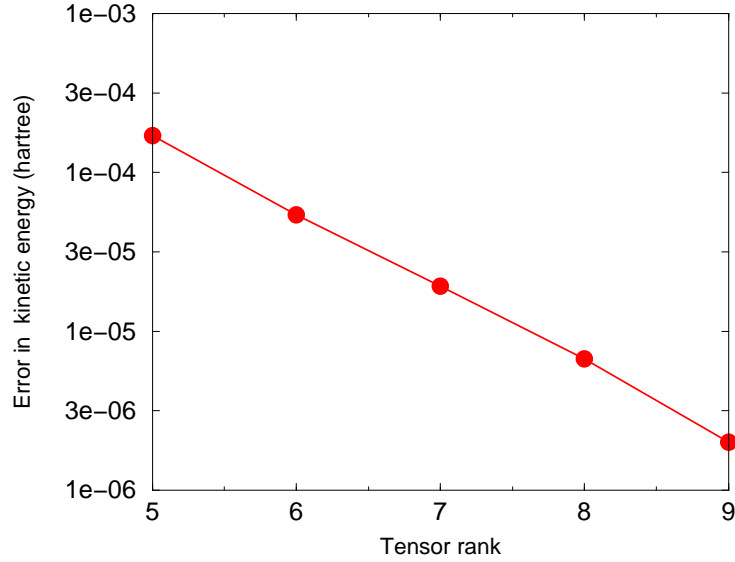


Figure 1: Error in the kinetic energy (hartree) versus tensor rank κ of the best tensor rank κ approximations for the H atom.

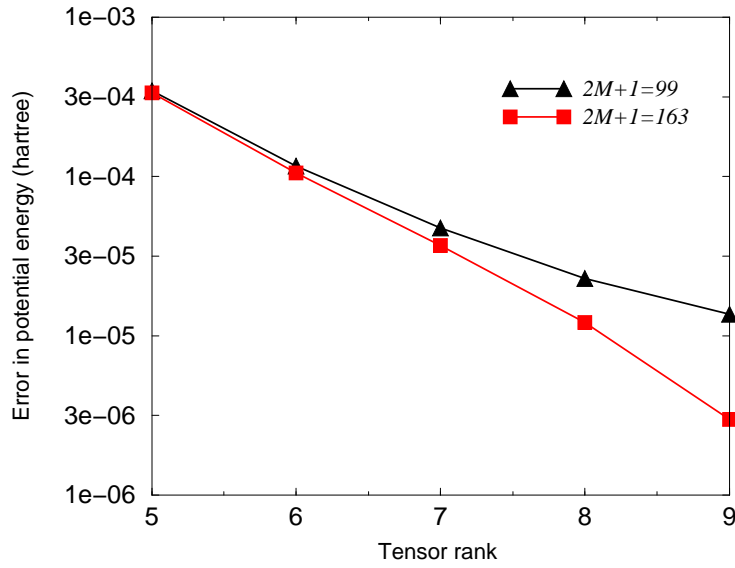


Figure 2: Error in the potential energy (hartree) versus tensor rank κ of the best tensor rank κ approximations for the H atom by using the different number of quadrature points $2M + 1$.

Eq. (25) is the potential energy obtained the best tensor rank κ approximation of the solution of the single-electron Schrödinger equation. The accuracy of the approximation depends on the number of quadrature points $2M + 1$ used to compute the integral (22). Fig. 2 shows the error in the potential energy for the best tensor rank κ approximation for varying κ for the H atom with different number of quadrature points. In order to get the accuracy of 3.0×10^{-6} hartree of the best tensor rank $\kappa = 9$ approximation, we had to use $2M + 1 = 163$ quadrature points. With the approximations of the kinetic energy and potential

energy of the H atom, we can get the best tensor rank κ approximations of the total energy by taking their sum. Then we can compare the quality of our approximations with the standard GTO bases. In order to compare our results, we need to have the energy of the H atom from the standard quantum chemistry GTO bases at the same rank. For this we compute the total energy of the H atom from Hackbusch’s bases [13] and also from the standard quantum chemistry GTO bases.

4 Accuracy of the total energy of the H atom

In this section, we present the error of the total energy of the H atom from the best tensor rank κ approximations and also from best radial Gaussian approximations of Hackbusch [13] at similar ranks. Hackbusch optimized the coefficients and exponents with respect to the weighted L^∞ norm. This is the so-called best radial Gaussian approximation. We present the total energy data from his bases and also from the standard quantum chemistry bases at same ranks. As we can see from Table 1, the energy of the H atom obtained from Hackbusch’s bases

Table 1: The total energy of the H atom from Hackbusch’s bases and also from the standard quantum chemistry bases at same ranks. The exact energy of the H atom is -0.5 hartree.

Rank	Energy of the H atom (hartree)	Name of the basis set
5	-0.49974836	Hackbusch
	-0.49929917	Dunning-SVP+
	-0.49933432	AVDZ
	-0.49980981	VTZ
6	-0.49992452	Hackbusch
	-0.49972903	Chipman
	-0.49982118	AVTZ
	-0.49994048	H06
7	-0.49997567	Hackbusch
	-0.49994832	AVQZ
	-0.49997607	H07
8	-0.49999166	Hackbusch
	-0.49994269	VANDUI
	-0.49997282	ROOS
9	-0.49999699	Hackbusch
	-0.49999478	AV5Z
	-0.49999652	H09

is fairly close to the energy from standard quantum chemistry basis sets. For particular ranks the total energy from his bases is even better. Now we can compare our best tensor rank κ approximations for the total energy of the H atom to the best radial Gaussian approximations [13] at the same rank. Once we have got the kinetic energy (10) and potential energy (25) from the best tensor rank κ approximations of the solution of the single-electron Schrödinger equation, we can get the best tensor rank κ approximations of the total energy for the H

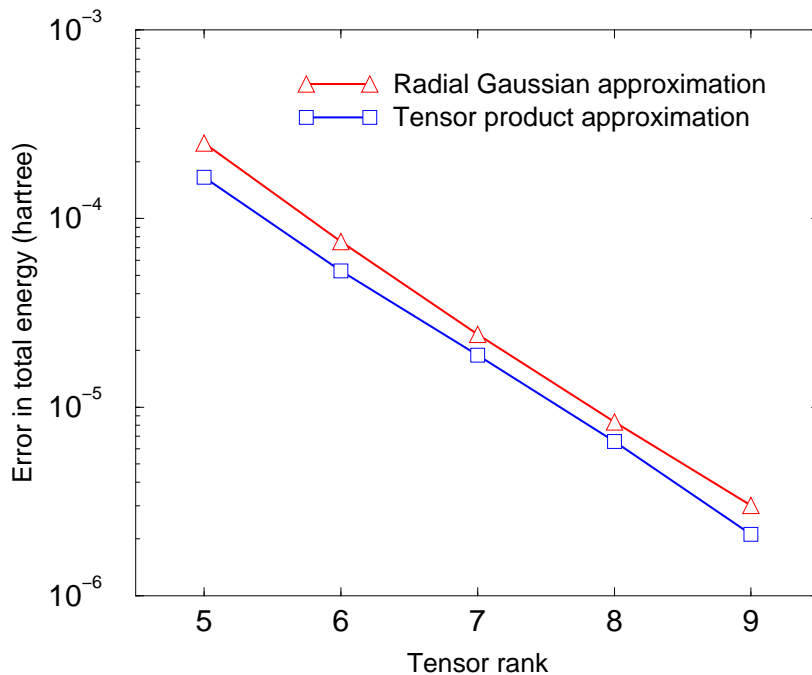


Figure 3: Error in the total energy (hartree) of the best tensor rank κ approximations and best radial Gaussian $L^\infty(\mathbb{R}_+)$ approximations for the H atom.

atom. Fig. 3 shows errors in the total energy of the best tensor rank κ approximations for the H atom. These are compared with the best radial Gaussian approximations of the same rank. As we can see from Fig. 3, both approaches give the same approximation errors. In fact, the best tensor rank κ approximation performs a little bit better. Hence our results indicate that the Gaussians already provide almost optimal approximations for the H atom. However, this does not seem to be the case for molecules with several nuclei as will be shown in the next section.

5 Single-electron systems with several nuclei

To study the accuracy of the total energy of single-electron systems with several nuclei, we consider positively charged ions like HHe^{2+} and H_3^{2+} and then solve the Schrödinger equation (1). In order to solve the Schrödinger equation within a Galerkin scheme, we use an uncontracted ($8s4p3d$) GTO basis for each atom with exponents taken from V5Z basis sets. Once we have calculated the wavefunctions of these systems, we obtain the best tensor rank $1 \leq \kappa \leq 15$ approximations for the above mentioned ions. Like in the case of the H atom, we compute the total energy from the best tensor rank κ approximations of the kinetic energy and potential energy. It should also be mentioned that the approximation error of the best tensor rank κ approximations might depend on the orientation of the ions with respect to the coordinate axes. A linear combination of two Gaussians with different centres and same exponents can be written as a rank-one tensor if they are oriented along an axis. Therefore the dimers H_2^+ , HHe^{2+} and a linear trimer H_3^{2+} are oriented along the diagonal in order to avoid such kind of rank reductions due to symmetry. Furthermore, we consider the triangular

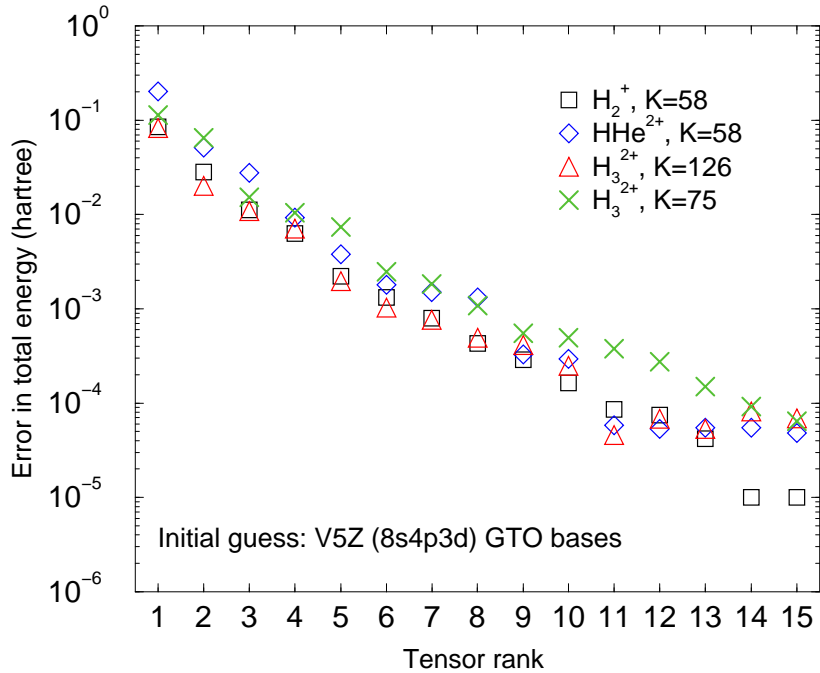


Figure 4: Error in the total energy (hartree) versus tensor rank κ of the best tensor rank κ approximations for various positively charged dimers H_2^+ ($K = 58$), HHe^{2+} ($K = 58$), and trimers H_3^{2+} ($K = 126$, triangle), H_3^{2+} ($K = 75$, linear). Nuclei are located on the diagonal or on the axes to form a triangle and the reference wavefunctions were calculated in an uncontracted V5Z GTO bases.

structure for H_3^{2+} with each nucleus located on an axis to form a triangle. Errors in the total energy of ions H_2^+ , HHe^{2+} and H_3^{2+} are shown in Fig. 4. As we can see from Fig. 4, the overall convergence rate for these systems is very similar. An error in total energy of $\leq 10^{-4}$ hartree can be achieved at tensor rank $\kappa \leq 15$. This error roughly corresponds to the basis set error of the GTO bases. This is a considerable reduction when we compare these tensor ranks κ with the initial ranks K of the GTO bases. The initial rank is $K = 58$ for H_2^+ , $K = 58$ for HHe^{2+} , $K = 75$ for the linear structure of H_3^{2+} and $K = 126$ for the triangular structure of H_3^{2+} .

6 The behaviour of the univariate components

We now want to show the behaviour of univariate components $h_k^{(i)}$ of Eq. (5) of the best tensor rank κ approximations for some single-electron systems. Fig. 5 shows the univariate components $h_k^{(1)}$ of the best tensor rank $\kappa = 5$ approximation for H_2^+ ion oriented along the x_3 -axis. The univariate components $h_k^{(3)}$ of the best tensor rank $\kappa = 5$ approximation are depicted in Fig. 6 where the H_2^+ ion oriented along the x_3 -axis. Fig. 7 shows the univariate components $h_k^{(1)}$ of the best tensor rank $\kappa = 5$ approximation for H_3^{2+} ion oriented along the diagonal. Here we want to mention that the behaviour of univariate components in x_1 -direction, x_2 -direction and x_3 -direction are the same if the ion is oriented along the diagonal.

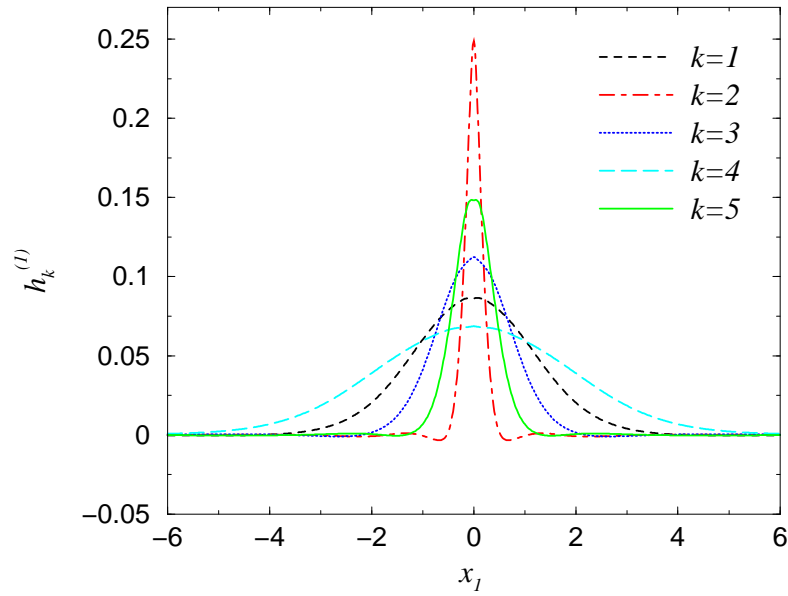


Figure 5: The univariate components $h_k^{(1)}(x_1)$ of the best tensor rank $\kappa = 5$ approximation for H_2^+ ion oriented along the x_3 -axis.

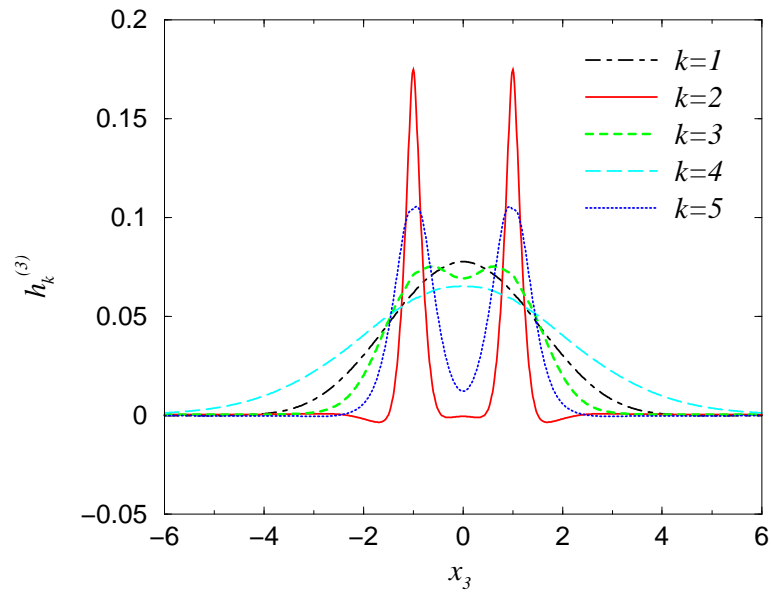


Figure 6: The univariate components $h_k^{(3)}(x_3)$ of the best tensor rank $\kappa = 5$ approximation for H_2^+ ion oriented along the x_3 -axis.

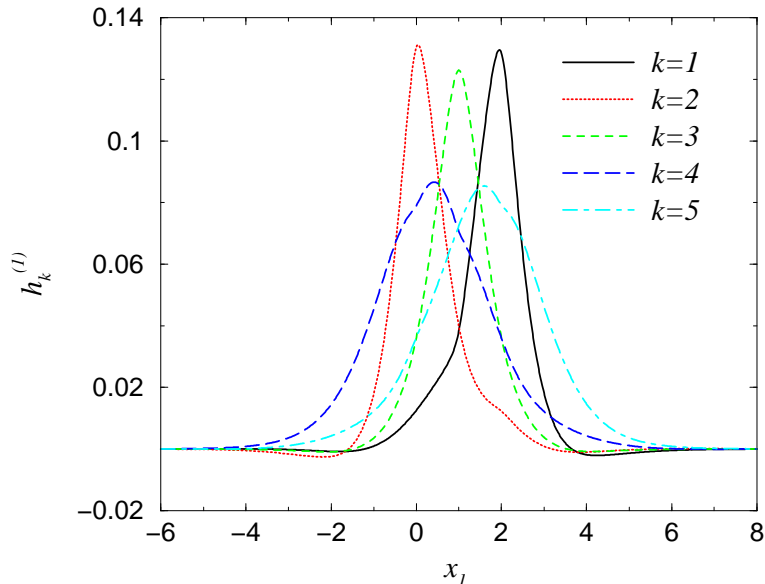


Figure 7: The univariate components $h_k^{(1)}(x_1)$ of the best tensor rank $\kappa = 5$ approximation for H_3^{2+} ion oriented along the diagonal.

7 The sparsity of univariate components

Sparsity of univariate components plays an important role to compute the integrals very efficiently. We therefore study the sparsity of univariate components $h_k^{(i)}$ of the TP approximation for the solution of the single-electron Schrödinger equation (1). One of the important aspects of the best tensor rank κ approximations is the sparse representation of univariate components $h_k^{(i)}$ of Eq. (5). So far the univariate components have been represented in the interpolating scaling function basis (4) on a uniform grid with the spacing $h = 2^{-j}$ bohr. It becomes rather inefficient for systems which contain heavy nuclei, because the resolution level j of Eq. (4) has to be adjusted such that our grid spacing $h = 2^{-j}$ bohr should be less than the standard deviation obtained from the largest exponent in the VDZ basis set. This criterion is necessary to deal with the electron-nuclear cusp. Therefore, instead of working with the scaling function representation of univariate components $h_k^{(i)}$, it is favourable to work with the wavelet representation where adaptive refinement is feasible. Besides, wavelets allow us to make a second compression step on univariate components $h_k^{(i)}$ for $i = 1, 2, 3$. For more details about wavelets, we refer to [8, 12].

7.1 Transformation of coefficients

Sometimes, it is convenient to switch between interpolating wavelet bases and Daubechies wavelet bases. For example, it is appropriate to approximate smooth functions by the so-called “interpolating scaling function” basis. But the corresponding biorthogonal wavelet basis turns out to be less convenient for certain computations within the tensor product format than orthogonal Daubechies wavelets. Therefore we transform the interpolating scaling

function coefficients of univariate components $h_k^{(i)}$ (5) along any direction to the scaling function coefficients in Daubechies wavelet bases. Then we perform the wavelet decomposition by using the Daubechies wavelet family of different degrees and study the sparsity of univariate components $h_k^{(i)}$. Now let us see how we can transform the scaling function coefficients of univariate components $h_k^{(i)}$ (5) to those in Daubechies wavelet bases,

$$h_k^{(i)}(x) = \sum_a C_{j,a} \phi_{j,a}(x) \approx \sum_b C'_{j,b} \phi'_{j,b}(x), \quad (26)$$

where $\phi_{j,a}(x) := 2^{j/2} \phi(2^j x - a)$, $a \in \mathbb{Z}$. $C_{j,a}$ are the univariate interpolating scaling function coefficients and $C'_{j,b}$ are the scaling function coefficients in Daubechies wavelet basis. To define $C'_{j,b}$, we project onto the Daubechies wavelet bases:

$$\sum_a C_{j,a} \int \phi_{j,a}(x) \phi'_{j,b}(x) dx = \sum_b C'_{j,b} \int \phi'_{j,b}(x) \phi'_{j,b}(x) dx. \quad (27)$$

If we use the orthonormality relation

$$\int \phi'_{j,b}(x) \phi'_{j,b'}(x) dx = \delta_{b,b'}, \quad b, b' \in \mathbb{Z} \quad (28)$$

then, Eq. (27) becomes

$$C'_{j,b} = \sum_a C_{j,a} \langle \phi'_{j,b} | \phi_{j,a} \rangle. \quad (29)$$

The overlap integrals $\langle \phi'_{j,b} | \phi_{j,a} \rangle$, can be computed by using the iterative method of Beylkin [2], Dahmen and Micchelli [7]. The refinement relations of scaling functions are used to get a linear system of equations for these integrals. Once we have obtained the linear system of equations, we can solve numerically. More details for the computation of such overlap integrals will be given in Appendix A.

7.2 Distribution of Daubechies wavelet coefficients

We present the distribution of Daubechies wavelet coefficients of univariate components $h_k^{(i)}$ at different resolution levels j for H_2^+ and H_3^{2+} ions. We also present the distribution of wavelet coefficients in different Daubechies wavelet bases, for instance, D10 and D18. Once we have obtained the scaling function coefficients (29) in Daubechies wavelet bases, we perform the wavelet decomposition and obtain Daubechies wavelet coefficients $d_{j,a}$ at different resolution levels j . Fig. 8 shows the spatial distribution of Daubechies wavelet coefficients of the univariate component $h_1^{(1)}(x_1)$ for H_2^+ ion oriented along the x_3 -axis, with the initial rank $K = 42$ and tensor rank $\kappa = 5$. Here we used the Daubechies wavelet family of degree $m = 10$, i.e., D10. It has $m/2$ vanishing moments and it can suppress the parts of the function which are polynomials up to the degree $m/2 - 1$. We also study the distribution of wavelet coefficients of the univariate components for other Daubechies wavelets, e.g., D18. The spatial distributions of wavelet coefficients for different Daubechies wavelets are shown in Fig. 9.

The spatial distribution of Daubechies wavelet coefficients of the univariate component $h_1^{(1)}(x_1)$, for H_3^{2+} ion oriented along the diagonal, is shown in Fig. 10 and the percentage of Daubechies wavelet coefficients is shown in Fig. 11. It can be seen from Fig. 8 to Fig. 10 that there are only a few significant coefficients at finer levels. Smaller values of j correspond to

coarser levels and larger values of j correspond to finer levels. When we go from a finer level to a next coarser level, the number of wavelet coefficients will be halved. It is clear from Fig. 11 that the percentage of wavelet coefficients $|d_{j,a}| > 10^{-6}$ decreases exponentially with respect to the resolution level j and there are only a few significant wavelet coefficients ($> 10^{-6}$) at finer resolution level $j = 5$. This is also the case for other single-electron systems. From these observations, one might construct an algorithm for the fast computation of various integrals involving orbitals, orbital products and electron density in electronic structure methods.

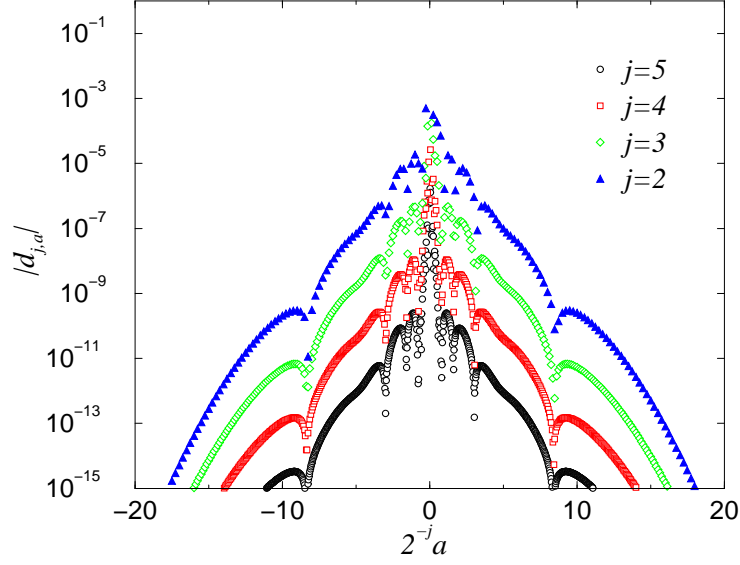


Figure 8: The spatial distribution of Daubechies wavelet coefficients of the univariate component $h_1^{(1)}(x_1)$ by using D10 for H_2^+ ion oriented along the x_3 -axis.

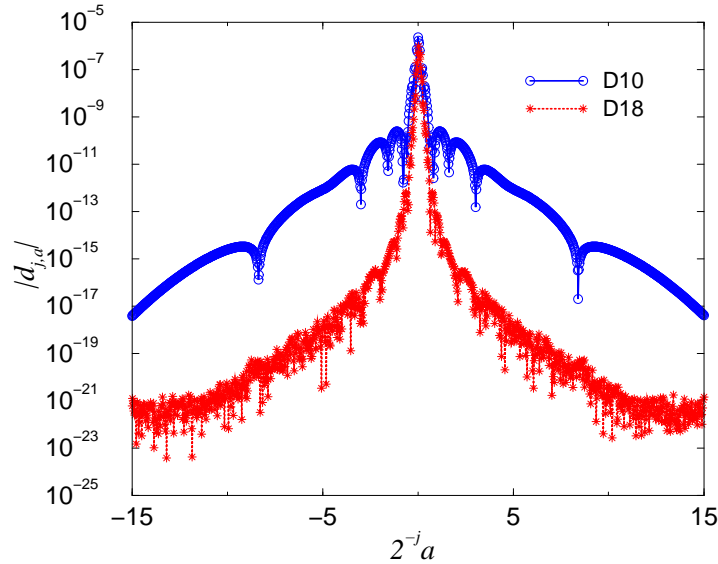


Figure 9: The spatial distribution of Daubechies wavelet coefficients of the univariate component $h_1^{(1)}(x_1)$ at $j = 5$ for H_2^+ ion oriented along x_3 -axis.

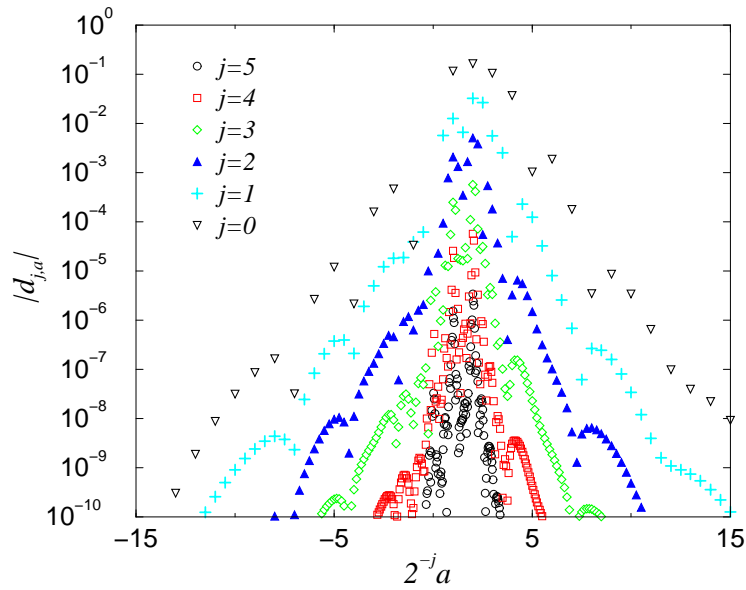


Figure 10: The spatial distribution of Daubechies wavelet coefficients of the univariate component $h_1^{(1)}(x_1)$ by using D10 for H_3^{2+} ion oriented along the diagonal.

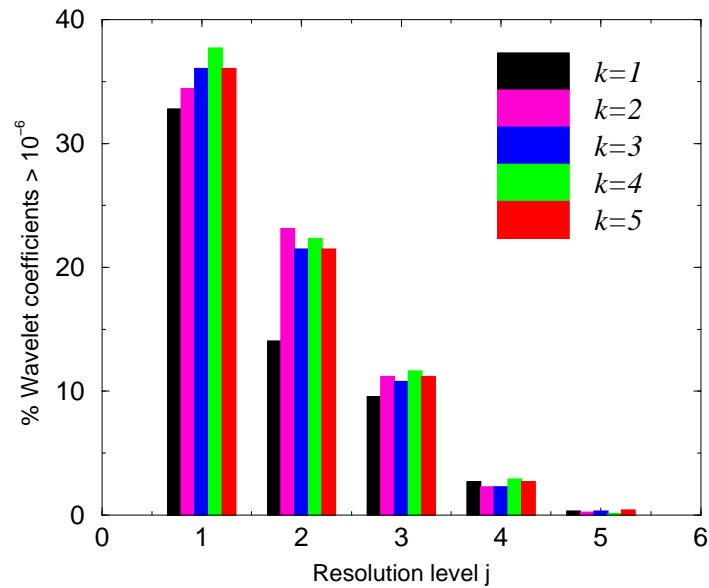


Figure 11: The percentage of Daubechies wavelet coefficients of the univariate components $h_k^{(1)}$ by using D10 for H_3^{2+} ion oriented along the diagonal. The percentage of Daubechies wavelet coefficients with $|d_{j,a}| > 10^{-6}$ is shown for different resolution levels j .

8 Conclusion

We have studied tensor product approximation of single-electron systems and also accuracy of the approximation. It turned out that the Gaussians already provide almost optimal approximations for the H atom. But this did not seem to be the case for molecules with several nuclei. We also studied the sparse wavelet representation of univariate components of the tensor product approximation. We observed that the percentage of wavelet coefficients decreases exponentially with respect to the resolution level and there are only a few significant wavelet coefficients at finer resolution levels. From these observations, one might construct algorithms for the fast computation of various integrals involving orbitals, orbital products and electron density in electronic structure methods.

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Appendix

A Computation of overlap and kinetic energy integrals

We use iterative method of Beylkin [2], Dahmen and Micchelli [7] to compute the overlap integrals (12) and kinetic energy integrals (11). The basic is to use filter coefficients [8, 12] and the scaling function relations, i.e., the integrals at resolution level j are related to the same kind of integrals at the next coarser resolution level $j-1$. Let us first assume the overlap integral

$$\begin{aligned} \langle \phi_{j,a} | \phi_{j,b} \rangle &= \int \phi_{j,a}(x) \phi_{j,b}(x) dx \\ &= \int 2^{j/2} \phi(2^j x - a) 2^{j/2} \phi(2^j x - b) dx. \end{aligned} \quad (30)$$

Now let $2^j x - b = \tilde{x}$, then

$$\begin{aligned} \langle \phi_{j,a} | \phi_{j,b} \rangle &= \int \phi(\tilde{x} - (a - b)) \phi(\tilde{x}) d\tilde{x} \\ &= \langle \phi_{0,a-b} | \phi_{0,0} \rangle \\ &= \langle \phi_{0,a'} | \phi_{0,0} \rangle, \end{aligned} \quad (31)$$

where $a' = a - b$. We can now use the refinement relation for scaling functions,

$$\phi(\tilde{x} - a') = 2 \sum_c h_c \phi(2\tilde{x} - 2a' - c) \quad (32)$$

and

$$\phi(\tilde{x}) = 2 \sum_e h_e \phi(2\tilde{x} - e). \quad (33)$$

Then the integral (31) becomes

$$\langle \phi_{0,a'} | \phi_{0,0} \rangle = 2^2 \sum_c \sum_e h_c h_e \int \phi(2\tilde{x} - 2a' - c) \phi(2\tilde{x} - e) d\tilde{x}, \quad (34)$$

now let $2\tilde{x} - e = x'$, then

$$\langle \phi_{0,a'} | \phi_{0,0} \rangle = 2 \sum_c \sum_e h_c h_e \int \phi(x' - 2a' - c + e) \phi(x') dx'. \quad (35)$$

Again let $-2a' - c + e = -b'$, then Eq. (35) becomes

$$\begin{aligned} \langle \phi_{0,a'} | \phi_{0,0} \rangle &= 2 \sum_{b'} \sum_e h_{b'-2a'+e} h_e \int \phi(x' - b') \phi(x') dx' \\ &= 2 \sum_{b'} \sum_e h_{b'-2a'+e} h_e \langle \phi_{0,b'} | \phi_{0,0} \rangle, \end{aligned} \quad (36)$$

where $h_{b'-2a'+e}$ and h_e are filter coefficients of Daubechies wavelet basis. Now Eq. (36) is a linear system of equations. Furthermore an additional condition

$$\sum_{a'} \langle \phi_{0,a'} | \phi_{0,0} \rangle = 1 \quad (37)$$

is required in order to obtain a unique solution to Eqs. (36), which corresponds to the overlap integrals (31). Eqs. (36) can be solved with the iterative process of Beylkin [2], Dahmen and Micchelli [7]. For this, we start with initial guesses $c_{a'}$ for the integrals $\langle \phi_{0,a'} | \phi_{0,0} \rangle$ which satisfy the condition (37), i.e.,

$$c_{a'}^{(0)} = \delta_{0,a'}. \quad (38)$$

With the guess $c_{a'}^{(m-1)}$, Eq. (36) leads to

$$c_{a'}^{(m)} = 2 \sum_{b'} \left(\sum_e h_{b'-2a'+e} h_e \right) c_{b'}^{(m-1)}. \quad (39)$$

In each iteration, the condition

$$\sum_{a'} c_{a'}^{(m)} = 1 \quad (40)$$

holds, i.e., the condition (37).

The same technique will be used to compute the kinetic energy integrals, i.e., $\langle \phi_{j,a_1} | \Delta_1 | \phi_{j,b_1} \rangle$. The linear system of equations

$$\langle \phi_{0,a'} | \Delta_1 | \phi_{0,0} \rangle = 2^3 \sum_{b'} \left(\sum_e h_{b'-2a'+e} h_e \right) \langle \phi_{0,b'} | \Delta_1 | \phi_{0,0} \rangle \quad (41)$$

has to satisfy the condition [2]

$$\sum_{a'} (a')^2 \langle \phi_{0,a'} | \Delta_1 | \phi_{0,0} \rangle = 2 \quad (42)$$

to compute the kinetic energy integrals. More details are also given in [10, 16].

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