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by

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Abstract The computation of two-electron integrals in electronic structure calculations is a major bottleneck in Hartree-Fock, density functional theory and post-Hartree-Fock methods. For large systems, one has to compute a huge number of two-electron integrals for these methods which leads to very high computational costs. The adaptive computation of products of orbitals in wavelet bases provides an important step towards efficient algorithms for the treatment of two-electron integrals in tensor product formats. For this, we use the non-standard approach of Beylkin which avoids explicit coupling between different resolution levels. We tested the efficiency of the algorithm for the products of orbitals in Daubechies wavelet bases and computed the two-electron integrals. This paper contains the detailed procedure and corresponding error analysis.

Keywords Standard approach · Non-standard approach · Daubechies wavelet bases · Tensor product approximation · Electronic structure calculations · Products of orbitals · Two-electron integrals

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1 Introduction

1.1 Two-electron integrals in electronic structure calculations

Over the past years, much work has been done in quantum chemistry to improve the efficiency of algorithms for electronic structure calculations. The most popular quantum many-particle models are Hartree-Fock, Møller-Plesset perturbation theory and coupled cluster theory, c.f., the monograph [29] for a detailed exposition of the subject. In these models, the many-electron wavefunctions are represented as linear combinations of anti-symmetric tensor products of single-electron wavefunctions, so-called orbitals, which reduces the computational complexity for the evaluation of matrix elements involving many-electron Hamiltonians and wavefunctions. According to Slater's rules, the $3N_e$ -dimensional integrals decompose into the familiar one- and two-electron integrals, where N_e is the number of electrons. The major computational task in electronic structure calculations therefore is the computation of two-electron integrals

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \Psi_a(\mathbf{x}) \Psi_b(\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{y}|} \Psi_c(\mathbf{y}) \Psi_d(\mathbf{y}) d\mathbf{x} d\mathbf{y}$$

over a set of orbitals $\{\Psi_a\}_{a \in A}$. If each orbital Ψ_a is represented in a common basis set $\{g_i\}_{i=1, \dots, K}$, then the two-electron integrals require computation of $\mathcal{O}(K^4)$ such integrals for the basis functions. This determines the computational complexity for small molecules especially if high accuracies are required. For large molecules, it is possible to benefit from locality for standard types of basis functions employed in quantum chemistry. A popular approach to reduce the computational complexity is to introduce another so-called auxiliary basis $\{\tilde{g}_i\}_{i=1, \dots, \tilde{K}}$ which can be used to approximate the

products of orbitals

$$\Psi_a \Psi_b = \sum_{i,j=1}^K c_{a,i} c_{b,j} g_i g_j \approx \sum_{i=1}^{\tilde{K}} \tilde{c}_{ab,i} \tilde{g}_i,$$

in two-electron integrals. Since the early work of Boys [8,9] and Preuss [38], atomic centred Cartesian-Gaussian functions became the most commonly used basis in electronic structure calculations. Efficient algorithms have been devised for the computation of the corresponding two-electron integrals [21,26,28,29,35,40,44]. Auxiliary bases were originally introduced for electron densities in the Hartree potential within density functional theory [2,20,33,41]. Later on, this approach was generalized to arbitrary two-electron integrals [30,37,45–48] where it reduces the computational complexity from $\mathcal{O}(K^4)$ to $\mathcal{O}(K^3)$. Successful applications have been reported for Møller-Plesset perturbation theory [4,23,49,50] and the coupled cluster method [39,42]. The latter is currently considered to be the most powerful model for highly accurate electronic structure calculations. Furthermore, we have to mention the closely related Cholesky decomposition of two-electron integrals [1,3,7] and the pseudospectral method [27,34] which can achieve a similar reduction of the computational complexity.

Within the present work, we focus on an alternative approach for the computation of two-electron integrals [11,12,31] which is based on the best fixed-rank tensor product approximation of orbitals. In a sense, our approach can be considered as a generalization of conventional Gaussian-type bases [11]. A crucial step is the computation of the pointwise product of factors in the tensor products representing the orbitals. It was shown in [10,12] that these factors are well approximated by Daubechies wavelets. Therefore, it suggests itself to perform these products directly in the wavelet bases, in order to benefit from adaptivity, while the computational complexity scales linearly with respect to the number of non-vanishing wavelet coefficients. For this purpose, various algorithms have been discussed in the literature. Besides Beylkin’s non-standard approach [5] which has been applied in the present work, we want to mention the work of Dahmen, Schneider and Xu [15]. Once the products have been computed, they can be further compressed by best fixed-rank tensor product approximations. This reduces the computational effort for the computation of two-electron integrals considerably as it has been discussed in Refs. [10–12]. We want to mention that such a compression step has been already suggested almost forty years ago by Dacre and Elder [13]. In their work, the fully optimized Gaussian expansions have been used to represent orbital products instead of more general tensor products which are considered below.

1.2 Tensor product approximation in electronic structure calculation

In consequence of our applications in electronic structure calculation, we have to deal with third-order tensors and their optimal tensor product approximations with fixed separation rank κ , so-called best rank- κ approximations. The tensors under consideration may represent individual orbitals and their products as well as the electron density or the corresponding Hartree potential. So far the concept of an orbital was not further specified in agreement with varied uses of this term in the chemistry literature. In the following we denote by an orbital a function in \mathbb{R}^3 which is used in the sense of a single-electron wavefunction and has the following properties: (i) locality, (ii) multi-scale character, (iii) smoothness up to pointwise singularities. Concerning locality we assume that the spread of orbitals is essentially independent of the size of the molecules. This requires the concept of local orbitals which forms the basis for all recent developments in the field of electronic structure calculations for large molecules, cf. [42, 50] and references therein. The orbitals of a molecule represent different length and energy scales, i.e., inner core orbitals, valence orbitals which form the actual chemical bonds, and virtual orbitals for the description of electron correlations in post-Hartree-Fock methods. Furthermore, orbitals have a well defined singular behaviour near atomic nuclei [25]. Altogether the properties (i) to (iii) provide our motivation for the tensor product approach where (ii) and (iii) strongly suggest the use of adaptive wavelet representations for the univariate factors of the tensor products.

For a given function $f(\mathbf{x})$ with $\mathbf{x} \in \mathbb{R}^3$, one can look for the best separable approximation with fixed rank κ in the following form

$$f(\mathbf{x}) \approx \sum_{k=1}^{\kappa} h_k^{(1)}(x_1) h_k^{(2)}(x_2) h_k^{(3)}(x_3), \quad (1)$$

where the univariate functions $h_k^{(i)}(x_i)$ for $i = 1, 2, 3$ are subject of the optimization. In particular, there are no orthogonality constraints imposed. Here the rank of a tensor is the smallest number of rank-one tensors whose linear combination represents the given tensor. The error of an approximation with fixed rank κ may be defined via the least-squares problem

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

This kind of variational problem is usually ill-posed, i.e., a minimizer does not always exist. In fact the space of

rank- κ tensor products is not closed in $L^2(\mathbb{R}^3)$ and in general an optimal solution for such a variational problem in dimension $d > 2$ does not exist [18]. However, it is possible to choose a set of functions $h_k^{(i)}(x_i)$ for which the error is arbitrarily close to σ_κ [22].

The variational problem (2) can be considerably simplified if we assume that the original function $f(\mathbf{x})$ is already given in tensor product format, for instance, canonical format [12] or Tucker format [31]. Usually orbitals are given as linear combinations of Cartesian-Gaussian functions. Therefore, one can take the advantage of such a nice representation to obtain best separable approximations for orbitals and related quantities. Given a function $f(\mathbf{x})$ which is represented in a Cartesian-Gaussian basis set as

$$f(\mathbf{x}) = \sum_{k=1}^K c_k \prod_{i=1}^3 g_k^{(i)}(x_i - A_k^{(i)}) \quad (3)$$

where

$$g_k^{(i)}(x_i - A_k^{(i)}) = (x_i - A_k^{(i)})_{k_i}^{(i)} e^{-\alpha_k(x_i - A_k^{(i)})^2}$$

for $i = 1, 2, 3$ and c_k are the coefficients including normalization constants. Here, K is the total number of Gaussians used to represent the function (3), the so-called initial separation rank. Then the individual univariate Gaussians are discretized on a uniform grid with grid spacing $h = 2^{-j}$,

$$g_k^{(i)}(x_i - A_k^{(i)}) \approx \sum_{a \in \Lambda} b_{k,j,a}^{(i)} \phi_{j,a}(x_i) \quad (4)$$

with $b_{k,j,a}^{(i)} = 2^{-j/2} g_k^{(i)}(2^{-j}a - A_k^{(i)})$. For this purpose, interpolating scaling functions $\phi_{j,a}(x) := 2^{j/2} \phi(2^j x - a)$ of Deslauriers and Dubuc [19] are used. Here $j \in \mathbb{Z}$, is the resolution level and $a \in \Lambda \subset \mathbb{Z}$, is the translation parameter. The size of the data vector used to represent each univariate Gaussian (4) is $N := \#\Lambda$. Then the discrete version of the function (3) in the tensor product format is given by

$$\tilde{\mathbf{f}} := \sum_{k=1}^K c_k \mathbf{b}_{k,j}^{(1)} \otimes \mathbf{b}_{k,j}^{(2)} \otimes \mathbf{b}_{k,j}^{(3)}, \quad (5)$$

where $\tilde{\mathbf{f}}$ is a coefficient tensor with initial separation rank K and $\mathbf{b}_{k,j}^{(i)} := \{b_{k,j,a}^{(i)}\}_{a=1}^N$, for $i = 1, 2, 3$ denotes the coefficient vectors in the expansion (4). For a given tensor with an initial separation rank $K \gg 1$, one can look for the best rank- κ approximation (1) with prescribed accuracy. The problem now becomes a minimization problem in the discrete tensor product format and the subsequent compression step is performed in a

purely algebraic manner using the discretized representation (5). The corresponding least-squares functional is

$$\sigma_\kappa(\tilde{\mathbf{f}}) := \inf_{\mathbf{h}_k^{(i)} \in \ell^2} \left\| \tilde{\mathbf{f}} - \sum_{k=1}^{\kappa} \mathbf{h}_k^{(1)} \otimes \mathbf{h}_k^{(2)} \otimes \mathbf{h}_k^{(3)} \right\|_{\ell^2}. \quad (6)$$

We want to mention, however, that for (bi)orthogonal wavelet and scaling function bases, a norm equivalence exists between L^2 and ℓ^2 which means that minimizing the discrete functional (6) in the tensor product format is equivalent to minimizing the continuous functional (2) up to a constant factor. Correspondingly one can obtain the best rank- κ approximation for products of orbitals $\Psi_a \Psi_b$ [10, 11] and in particular for the electron density to compute the Hartree potential in an efficient way [12] by using appropriate tensor product approximations for the Coulomb potential.

In the present work, we focus on efficient algorithms for the computation of products of orbitals which are already represented by best rank- κ tensor product approximations. This is a preparatory step and the resulting rank- κ^2 tensor products are further compressed and used for the calculation of two-electron integrals.

1.3 Various approaches to deal with products of orbitals

In principle, one can use the best rank- κ approximation of orbitals Ψ_a and compute their products $\Psi_a \Psi_b$ directly on the grid. This is what we call the direct approach for orbital products. On high resolution grids, the direct approach is rather costly to treat two-electron integrals. Instead, we want to have an algorithm that takes the advantage of adaptivity and computes the products more efficiently. Precisely, we want to compute only significant contributions on the different length-scales and neglect the smaller contributions up to a certain threshold ϵ . According to Eq. (4), the univariate factors $h_k^{(i)}(x_i)$ for $i = 1, 2, 3$ of the tensor product approximations of the individual orbitals are represented by interpolating scaling functions of Deslauriers and Dubuc [19]. In an intermediate step we convert the factors into orthogonal Daubechies wavelet bases and perform a subsequent compression step. The computation of products of factors in a hierarchical wavelet bases with optimal complexity, i.e., linear with respect to the number of non-zero wavelet coefficients, can be achieved via different algorithms. In the following, we want to discuss the so-called standard approach, a straightforward method simply taking the product of the wavelet expansions, and Beylkin's non-standard approach [5]. The latter avoids explicit coupling between different resolution

levels. To the best of our knowledge, numerical results for the non-standard approach have not been presented so far in the literature. In this paper, we present results for products of orbitals of the C_2H_6 molecule. We studied the computational complexity of the non-standard approach with different Daubechies wavelet bases [16, 17] and tested the accuracy of resulting two-electron integrals by comparison with direct orbital products in Section 6.

2 Non-standard approach for the computation of products of orbitals

In the following, we want to compare the performance of the standard and non-standard approach for the computation of products of functions represented in wavelet bases. The fundamental difference is that the standard approach deals with products of wavelets at different resolution levels whereas in Beylkin's non-standard approach [5], products of wavelets and scaling functions appear only on the same resolution level.

2.1 Standard approach

Let us consider two functions

$$f = \sum_{a \in \Lambda_n} s_{n,a}^{(1)} \phi_{n,a}, \quad \text{and} \quad g = \sum_{a \in \Lambda_n} s_{n,a}^{(2)} \phi_{n,a},$$

represented by scaling functions $\phi_{n,a}$ at the resolution level n , where $a \in \Lambda_n \subset \mathbb{Z}$ is the translation parameter. The size of the data vector used to represent each of these functions is $N := \#\Lambda_n$. Here $s_{n,a}^{(1)}$ and $s_{n,a}^{(2)}$ are the scaling function coefficients of f and g , respectively. The multiresolution representations of these functions in the wavelet basis are

$$f = \sum_{a \in \Lambda_{j_0}} s_{j_0,a}^{(1)} \phi_{j_0,a} + \sum_{j=j_0}^{n-1} \sum_{a \in \Lambda_j} d_{j,a}^{(1)} \psi_{j,a}, \quad (7)$$

and

$$g = \sum_{a \in \Lambda_{j_0}} s_{j_0,a}^{(2)} \phi_{j_0,a} + \sum_{j=j_0}^{n-1} \sum_{a \in \Lambda_j} d_{j,a}^{(2)} \psi_{j,a}, \quad (8)$$

where $d_{j,a}^{(1)}$ and $d_{j,a}^{(2)}$ are the wavelet coefficients corresponding to f and g , respectively and j_0 is the coarsest resolution level. The product of two functions f and g

in the standard approach becomes

$$\begin{aligned} fg &= \sum_{j=j_0}^{n-1} \sum_{j'=j_0}^{n-1} \sum_{a \in \Lambda_j} \sum_{a' \in \Lambda_{j'}} d_{j,a}^{(1)} d_{j',a'}^{(2)} \psi_{j,a} \psi_{j',a'} \\ &+ \sum_{j=j_0}^{n-1} \sum_{a \in \Lambda_j} \sum_{a' \in \Lambda_{j_0}} d_{j,a}^{(1)} s_{j_0,a'}^{(2)} \psi_{j,a} \phi_{j_0,a'} \\ &+ \sum_{j'=j_0}^{n-1} \sum_{a \in \Lambda_{j_0}} \sum_{a' \in \Lambda_{j'}} s_{j_0,a}^{(1)} d_{j',a'}^{(2)} \phi_{j_0,a} \psi_{j',a'} \\ &+ \sum_{a \in \Lambda_{j_0}} \sum_{a' \in \Lambda_{j_0}} s_{j_0,a}^{(1)} s_{j_0,a'}^{(2)} \phi_{j_0,a} \phi_{j_0,a'}, \end{aligned} \quad (9)$$

where we can observe interactions between different resolution levels. As Daubechies wavelets have compact support, the algorithm leads to $\mathcal{O}(N \log_2 N)$ computational complexity. Here, we estimate the computational complexity by computing the total number of non-zero products in the expansion (9) without taking into account possible compressions of the wavelet expansions (7) and (8).

2.2 Non-standard approach

The non-standard approach of Beylkin [5] avoids explicit coupling between different resolution levels for the product. In order to uncouple the interaction between resolution levels, Beylkin suggested not to use the full wavelet expansions of the functions (7) and (8). Instead, one should use wavelet expansions of the functions f and g only up to the next coarser level before taking their product. Let us assume that the functions f and g are given at resolution level n . We can express these functions in wavelet and scaling functions at the next coarser level $n-1$ as

$$f = \sum_{a \in \Lambda_{n-1}} s_{n-1,a}^{(1)} \phi_{n-1,a} + \sum_{a \in \Lambda_{n-1}} d_{n-1,a}^{(1)} \psi_{n-1,a}, \quad (10)$$

and

$$g = \sum_{a \in \Lambda_{n-1}} s_{n-1,a}^{(2)} \phi_{n-1,a} + \sum_{a \in \Lambda_{n-1}} d_{n-1,a}^{(2)} \psi_{n-1,a}. \quad (11)$$

The product of two functions (10) and (11) becomes

$$fg = F_1^{n-1} + F_2^{n-1} + F_3^{n-1} + F_4^{n-1}, \quad (12)$$

where

$$F_1^{n-1} = \sum_{a \in \Lambda_{n-1}} \sum_{a' \in \Lambda_{n-1}} s_{n-1,a}^{(1)} s_{n-1,a'}^{(2)} \phi_{n-1,a} \phi_{n-1,a'},$$

$$F_2^{n-1} = \sum_{a \in \Lambda_{n-1}} \sum_{a' \in \Lambda_{n-1}} s_{n-1,a}^{(1)} d_{n-1,a'}^{(2)} \phi_{n-1,a} \psi_{n-1,a'},$$

$$F_3^{n-1} = \sum_{a \in \Lambda_{n-1}} \sum_{a' \in \Lambda_{n-1}} d_{n-1,a}^{(1)} s_{n-1,a'}^{(2)} \psi_{n-1,a} \phi_{n-1,a'},$$

$$F_4^{n-1} = \sum_{a \in \Lambda_{n-1}} \sum_{a' \in \Lambda_{n-1}} d_{n-1,a}^{(1)} d_{n-1,a'}^{(2)} \psi_{n-1,a} \psi_{n-1,a'}.$$

Here the last three combinations F_2^{n-1} , F_3^{n-1} and F_4^{n-1} contain one or two wavelets in the product. It should be mentioned that most of the wavelet coefficients $d_{n-1,a}$ are assumed to be small at higher resolution levels. Therefore, the last three combinations F_2^{n-1} , F_3^{n-1} and F_4^{n-1} are considered to be sparse in a sense that one can apply an adaptive thresholding procedure to avoid the computation of small contributions. However, the first combination F_1^{n-1} is not small because it consists of products of scaling functions. In order to achieve some sparsity for F_1^{n-1} , the scaling functions are expressed in wavelets and scaling functions at the next coarser level $n-2$. Then F_1^{n-1} can be further decomposed into

$$F_1^{n-1} = F_1^{n-2} + F_2^{n-2} + F_3^{n-2} + F_4^{n-2}.$$

This decomposition can be repeated on each level until the coarsest level j_0 is reached. The product of functions (12) can be rewritten as

$$fg = \sum_{a \in \Lambda_{j_0}} \sum_{a' \in \Lambda_{j_0}} s_{j_0,a}^{(1)} s_{j_0,a'}^{(2)} \phi_{j_0,a} \phi_{j_0,a'} + \sum_{j=j_0}^{n-1} \sum_{a \in \Lambda_j} \sum_{a' \in \Lambda_j} s_{j,a}^{(1)} d_{j,a'}^{(2)} \phi_{j,a} \psi_{j,a'} + \sum_{j=j_0}^{n-1} \sum_{a \in \Lambda_j} \sum_{a' \in \Lambda_j} d_{j,a}^{(1)} s_{j,a'}^{(2)} \psi_{j,a} \phi_{j,a'} + \sum_{j=j_0}^{n-1} \sum_{a \in \Lambda_j} \sum_{a' \in \Lambda_j} d_{j,a}^{(1)} d_{j,a'}^{(2)} \psi_{j,a} \psi_{j,a'}, \quad (13)$$

where products of scaling functions and wavelets are at the same resolution level. We still need to do something more in order to get the final wavelet representation. For this, let us start with the Haar wavelet, i.e., D2 basis which provides a simple illustration to the general case of Daubechies wavelets. The product of wavelets and scaling functions in the Haar basis is non-zero only for $a = a'$ and we have the following explicit relations

$$\phi_{j,a} \phi_{j,a} = 2^{j/2} \phi_{j,a}, \quad (14)$$

$$\phi_{j,a} \psi_{j,a} = 2^{j/2} \psi_{j,a}, \quad (15)$$

$$\psi_{j,a} \psi_{j,a} = 2^{j/2} \phi_{j,a}. \quad (16)$$

Using these relations, Eq. (13) becomes

$$fg = \sum_{a \in \Lambda_{j_0}} \hat{s}_{j_0,a} \phi_{j_0,a} + \sum_{j=j_0}^{n-1} \sum_{a \in \Lambda_j} \hat{d}_{j,a} \psi_{j,a} + \sum_{j=j_0+1}^{n-1} \sum_{a \in \Lambda_j} \hat{r}_{j,a} \phi_{j,a}, \quad (17)$$

where

$$\hat{s}_{j_0,a} = 2^{j_0/2} [s_{j_0,a}^{(1)} s_{j_0,a}^{(2)} + d_{j_0,a}^{(1)} d_{j_0,a}^{(2)}],$$

$$\hat{d}_{j,a} = 2^{j/2} [s_{j,a}^{(1)} d_{j,a}^{(2)} + d_{j,a}^{(1)} s_{j,a}^{(2)}],$$

$$\hat{r}_{j,a} = 2^{j/2} d_{j,a}^{(1)} d_{j,a}^{(2)}.$$

As the third term of Eq. (17) is still in the scaling function representation, we need to expand it into the wavelet basis with scaling function coefficients $\bar{s}_{j_0,a}$ and wavelet coefficients $\bar{d}_{j,a}$. We then end up with the following expression

$$fg = \sum_{a \in \Lambda_{j_0}} (\hat{s}_{j_0,a} + \bar{s}_{j_0,a}) \phi_{j_0,a} + \sum_{j=j_0}^{n-1} \sum_{a \in \Lambda_j} (\hat{d}_{j,a} + \bar{d}_{j,a}) \psi_{j,a}.$$

which represents the expansion of a product of functions in the Haar basis. A similar procedure can be used for the standard approach (9).

In order to check the computational complexity for a product of functions in the Haar basis, we consider two Gaussian functions with exponents 4 and 8 on the unit interval and compute their product by using the standard and non-standard algorithms. The total number of non-zero products we need to compute in both algorithms are shown in Fig. 1 a). As can be seen from Fig. 1 a), we just need to compute a much smaller number of products in the non-standard algorithm compared to the standard algorithm. We also show the total number of products which have absolute coefficients greater than a threshold ϵ for the standard and non-standard algorithms in Fig. 1 b) and c), respectively. It can be seen that the non-standard algorithm remains more efficient using adaptive thresholding procedures to avoid the computation of small contributions. For our envisaged applications in electronic structure calculations, we therefore restrict ourselves to the non-standard algorithm.

In the Haar wavelet case, everything is simple since we have explicit relations, cf. Eqs. (14) to (16), for products of scaling functions and wavelets. In the general case of Daubechies wavelets, such explicit relations do not exist anymore, because Daubechies wavelets are not closed under multiplication. Therefore, we have to approximate the products, i.e., $\phi_{j_0,a} \phi_{j_0,a'}$, $\phi_{j,a} \psi_{j,a'}$ etc., in the wavelet basis. The first product can be represented as

$$\phi_{j_0,a} \phi_{j_0,a'} = \sum_{i \in \Lambda_{j_0}} S_{VVV}^{j_0,j_0}(a, a', i) \phi_{j_0,i} + \sum_{l \geq j_0} \sum_{i \in \Lambda_l} D_{VVW}^{j_0,l}(a, a', i) \psi_{l,i}. \quad (18)$$

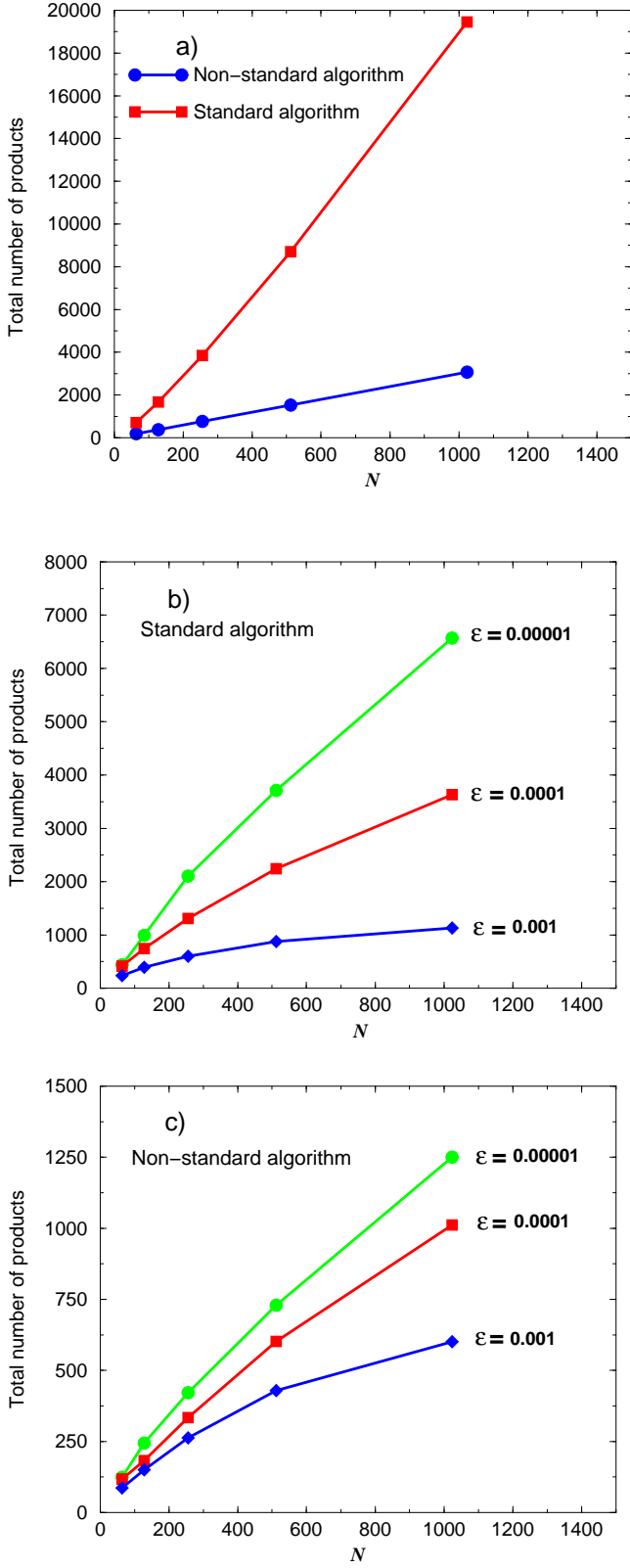


Fig. 1 Computational complexity for the product of two Gaussian functions in the Haar wavelet basis using the standard and non-standard algorithms versus the number of grid points N on the finest resolution level. b) and c) show the number of products which have absolute values of the coefficients greater than the threshold ϵ .

Using orthonormality of Daubechies wavelets, we get

$$S_{VVV}^{j_0, j_0}(a, a', i) = \int_{\mathbb{R}} \phi_{j_0, a}(x) \phi_{j_0, a'}(x) \phi_{j_0, i}(x) dx,$$

and

$$D_{VVW}^{j_0, l}(a, a', i) = \int_{\mathbb{R}} \phi_{j_0, a}(x) \phi_{j_0, a'}(x) \psi_{l, i}(x) dx.$$

In the following we refer to these integrals as coupling coefficients. By inserting coupling coefficients in the first term of Eq. (13), we form the sums

$$\tilde{F}_1^{j_0}(i) = \sum_{a \in \Lambda_{j_0}} \sum_{a' \in \Lambda_{j_0}} s_{j_0, a}^{(1)} s_{j_0, a'}^{(2)} S_{VVV}^{j_0, j_0}(a, a', i)$$

$$F_1^{j_0}(l, i) = \sum_{a \in \Lambda_{j_0}} \sum_{a' \in \Lambda_{j_0}} s_{j_0, a}^{(1)} s_{j_0, a'}^{(2)} D_{VVW}^{j_0, l}(a, a', i)$$

with respect to scaling function and wavelet coefficients.

Now let us take the second term of Eq. (13) and represent the product $\phi_{j, a} \psi_{j, a'}$ as we did in the previous case,

$$\begin{aligned} \phi_{j, a} \psi_{j, a'} &= \sum_{i \in \Lambda_j} S_{VVV}^{j, j}(a, a', i) \phi_{j, i} \\ &+ \sum_{l \geq j} \sum_{i \in \Lambda_l} D_{VWV}^{j, l}(a, a', i) \psi_{l, i}. \end{aligned} \quad (19)$$

As before, we obtain the coupling coefficients

$$S_{VVV}^{j, j}(a, a', i) = \int_{\mathbb{R}} \phi_{j, a}(x) \psi_{j, a'}(x) \phi_{j, i}(x) dx,$$

and

$$D_{VWV}^{j, l}(a, a', i) = \int_{\mathbb{R}} \phi_{j, a}(x) \psi_{j, a'}(x) \psi_{l, i}(x) dx.$$

Once more, we can form the sums

$$\tilde{F}_2^j(i) = \sum_{a \in \Lambda_j} \sum_{a' \in \Lambda_j} s_{j, a}^{(1)} d_{j, a'}^{(2)} S_{VVV}^{j, j}(a, a', i),$$

$$F_2^j(l, i) = \sum_{a \in \Lambda_j} \sum_{a' \in \Lambda_j} s_{j, a}^{(1)} d_{j, a'}^{(2)} D_{VWV}^{j, l}(a, a', i), \quad (20)$$

for the second term of Eq. (13). The remaining terms of Eq. (13) can be handled in a similar way. Here we also need the coupling coefficients

$$S_{WVV}^{j, j}(a, a', i) = \int_{\mathbb{R}} \psi_{j, a}(x) \psi_{j, a'}(x) \phi_{j, i}(x) dx,$$

and

$$D_{WVV}^{j, l}(a, a', i) = \int_{\mathbb{R}} \psi_{j, a}(x) \psi_{j, a'}(x) \psi_{l, i}(x) dx.$$

A simple algorithm to compute the coupling coefficients is the iterative method of Beylkin [6], Dahmen and Micchelli [14]. In Fig. 2 a) to c), we show the decay

of the coupling coefficients for different combinations of scaling functions and wavelets. For this, we compute the maximum values of coupling coefficients, e.g.,

$$\|D_{VW}^{j,l}\|_{\infty} := \max\left\{D_{VW}^{j,l}(a, a', i) : a, a', i \in \mathbb{Z}\right\},$$

for different Daubechies wavelet bases D4, D8 and D10. Here, D_m stands for the Daubechies wavelet family of degree m . D_m has $m/2$ vanishing moments and represents polynomial up to degree $m/2 - 1$. The maximum values of the coupling coefficients can be estimated by

$$\|D_{VW}^{j,l}\|_{\infty} \leq c 2^{-s(l-j)} 2^{\frac{1}{2}j}, \quad (21)$$

for $0 \leq s < \min\{t, p\}$ where t denotes the Sobolev regularity of the wavelet, i.e., $t := \sup\{s : \psi \in H^s\}$ and p refers to the number of vanishing moments, cf. Ref. [32] for further details. By taking the Sobolev regularity of Daubechies wavelets from Ref. [36], it turns out that this estimate provides a good description for the decay of coupling coefficients, with increasing resolution level l , shown in Fig. 2 a) to c).

The product of two functions in the general case of Daubechies wavelets using the non-standard approach becomes

$$\begin{aligned} fg &= \sum_j \sum_{i \in \Lambda_j} \left(\tilde{F}_1^{j_0}(i) \delta_{j,j_0} + \tilde{F}_2^j(i) \right. \\ &\quad \left. + \tilde{F}_3^j(i) + \tilde{F}_4^j(i) \right) \phi_{j,i} \\ &+ \sum_l \sum_{i \in \Lambda_l} \left[\sum_{j \leq l} \left(F_1^j(l, i) + F_2^j(l, i) \right. \right. \\ &\quad \left. \left. + F_3^j(l, i) + F_4^j(l, i) \right) \right] \psi_{l,i}. \end{aligned} \quad (22)$$

What remains to be done is to decompose the scaling functions $\phi_{j,i}$ on levels $j > j_0$ into wavelets and to add up the corresponding contributions to the wavelet part of Eq. (22).

3 Contraction of scaling function contributions

For the computation of the product of two functions which are both smooth except for possibly a few isolated singularities, it is beneficial to perform the double sum (20) by first summing over the scaling function coefficients, i.e.,

$$F_2^j(l, i) = \sum_{a' \in \Lambda_j} d_{j,a'}^{(2)} \left(\sum_{a \in \Lambda_j} s_{j,a}^{(1)} D_{VW}^{j,l}(a, a', i) \right), \quad (23)$$

where the sum in brackets is given by

$$\int_{\mathbb{R}} \left(\sum_{a \in \mathcal{J}_{l,i}} s_{j,a}^{(1)} \phi_{j,a}(x) \right) \psi_{j,a'}(x) \psi_{l,i}(x) dx.$$

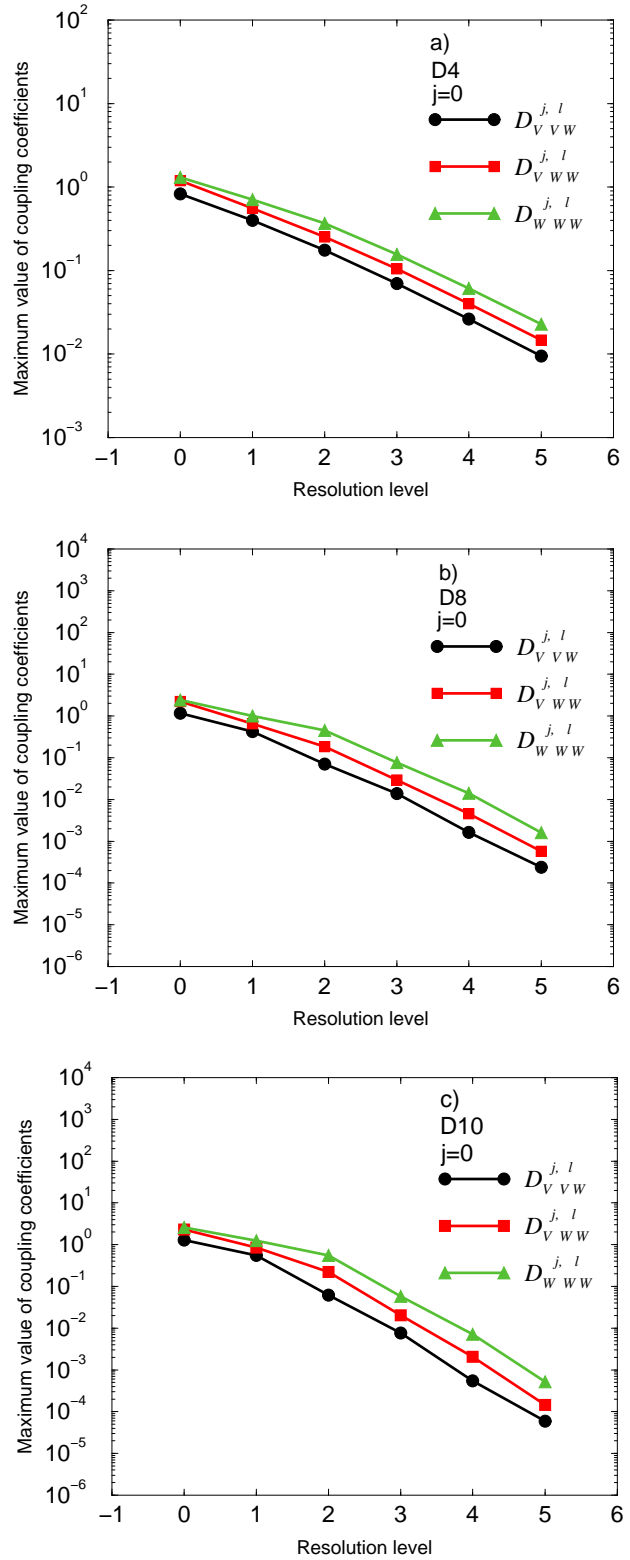


Fig. 2 The maximum values of coupling coefficients at different resolution levels l for Daubechies wavelets with various number of vanishing moments.

The sum of scaling functions, which runs over the index set

$$\mathcal{I}_{l,i} := \{a \in \mathbb{Z} : \text{supp}\psi_{l,i} \cap \text{supp}\phi_{j,a} \neq \emptyset\},$$

corresponds to

$$g|_{\text{supp}\psi_{l,i}} \approx \sum_{a \in \mathcal{I}_{l,i}} s_{j,a}^{(1)} \phi_{j,a}, \quad \text{with } s_{j,a}^{(1)} = \int_{\mathbb{R}} g(x) \phi_{j,a}(x) dx.$$

Let us assume $g \in C^\infty(\text{supp}\psi_{l,i})$ and perform a Taylor expansion of g at the centre of $\psi_{l,i}$ (p vanishing moments) which gives

$$g(x)|_{\text{supp}\psi_{l,i}} = \sum_{m=0}^{p-1} a_m (x-x_0)^m + R_{p-1}(x),$$

where the remainder of the Taylor series can be represented by the integral

$$R_{p-1}(x) = \frac{(x-x_0)^p}{(p-1)!} \int_0^1 (1-t)^{p-1} g^{(p)}(x_0 + t(x-x_0)) dt.$$

Next, we split the scaling function coefficients into

$$s_{j,a}^{(1)} = \tilde{s}_{j,a}^{(1)} + \Delta s_{j,a}^{(1)}$$

with

$$\tilde{s}_{j,a}^{(1)} := \int_{\mathbb{R}} \left(\sum_{m=0}^{p-1} a_m (x-x_0)^m \right) \phi_{j,a}(x) dx$$

and

$$\Delta s_{j,a}^{(1)} := \int_{\mathbb{R}} R_{p-1}(x) \phi_{j,a}(x) dx.$$

A straightforward estimate gives

$$|\Delta s_{j,a}^{(1)}| \lesssim 2^{-(p+\frac{1}{2})j} \|g\|_{W_\infty^p(\Omega_{l,i})}$$

with $\Omega_{l,i} := \cup_{a \in \mathcal{I}_{l,i}} \text{supp}\phi_{j,a}$. Together with (21), we obtain

$$\left| \sum_{a \in \mathcal{I}_{l,i}} \Delta s_{j,a}^{(1)} D_{VWW}^{j,l}(a, a', i) \right| \lesssim 2^{-s(l-j)} 2^{-pj} \|g\|_{W_\infty^p(\Omega_{l,i})}$$

for $0 \leq s < \min\{t, p\}$ where t denotes the Sobolev regularity of the wavelet. Because the scaling functions exactly represent polynomials of degree $p-1$, we get

$$\sum_{a \in \mathcal{I}_{l,i}} \tilde{s}_{j,a}^{(1)} \phi_{j,a}(x) \Big|_{\text{supp}\psi_{l,i}} = \sum_{m=0}^{p-1} a_m (x-x_0)^m.$$

From this and the following estimate

$$\begin{aligned} & \left| \int_{\mathbb{R}} \psi_{j,a'}(x) (x-x_0)^m \psi_{l,i}(x) dx \right| \\ & \lesssim 2^{-(s+\frac{1}{2})l} \|(\cdot-x_0)^m \psi_{j,a'}\|_{W_\infty^s(\text{supp}\psi_{l,i})} \\ & \lesssim 2^{-(s+\frac{1}{2})l} \sum_{\substack{\alpha_1+\alpha_2 \leq s \\ \alpha_1 \leq m}} 2^{-(m-\alpha_1)l} \|\psi_{j,a'}\|_{W_\infty^{\alpha_2}} \\ & \lesssim 2^{-(s+\frac{1}{2})l} \sum_{\substack{\alpha_1+\alpha_2 \leq s \\ \alpha_1 \leq m}} 2^{-(m-\alpha_1)l} 2^{(\alpha_2+\frac{1}{2})j} \\ & \lesssim \begin{cases} 2^{-(s+\frac{1}{2})(l-j)} 2^{-mj} & \text{if } m \leq s \\ 2^{-(m+\frac{1}{2})l} 2^{\frac{1}{2}j} & \text{if } m > s \end{cases}, \end{aligned}$$

we obtain the final estimate

$$\begin{aligned} & \left| \sum_{a \in \mathcal{I}_j} s_{j,a}^{(1)} D_{VWW}^{j,l}(a, a', i) \right| \tag{24} \\ & \lesssim \left(2^{-(s+\frac{1}{2})(l-j)} 2^{-j} + 2^{-s(l-j)} 2^{-pj} \right) \|g\|_{W_\infty^p(\Omega_{l,i})}, \end{aligned}$$

where $\int_{\mathbb{R}} \psi_{j,a'}(x) \psi_{l,i}(x) dx = 0$ has been assumed. For comparison, this estimate decays for $l \leq (2p-1)j$ by $\mathcal{O}(2^{-\frac{1}{2}l} 2^{-j})$ faster than the uncontracted estimate (21).

We want to mention that the idea to smoothen one factor by contraction has already been discussed in a qualitative manner by Beylkin [5].

4 Adaptivity

In order to compensate for the computational overhead of the non-standard approach, it is mandatory to use adaptivity. This has been already demonstrated for the Haar wavelet in Fig. 1. For our envisaged application, the sparsity of wavelet approximations for tensor product factors has been demonstrated in Ref. [12]. In addition, it is possible to use the contraction scheme discussed in Section 3 to further reduce the magnitude of the mixed contributions represented by the sums F_2^j and F_3^j in the expansion (22) according to the estimate (24). It remains to devise an adaptive algorithm to compute only those contributions in (22) which are greater than a certain threshold ϵ . A simple approach is to perform a hierarchical decomposition of the domain and to compute the maximum norm of the coefficients on each sub domain. Then one can easily devise a tree like algorithm which decides whether specific hierarchical subsets of the index set in the sum (23) potentially contain contributions which are greater than the threshold.

A simple example which illustrates the potential of adaptivity in electronic structure calculations is the product of the functions

$$f(x) = e^{-4|x|}, \quad g(x) = e^{-8|x|}, \quad x \in [-20, 20].$$

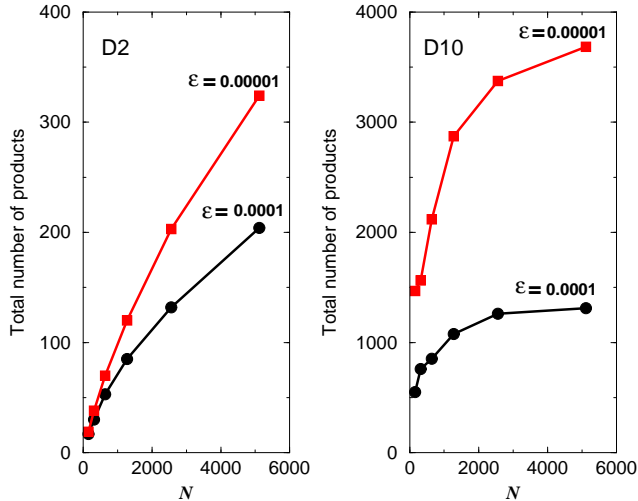


Fig. 3 Computational complexity of the non-standard algorithm for the product of two Slater-type functions in D2 and D10 wavelet bases versus the number of grid points N on the finest resolution level.

These functions resemble to the familiar Slater-type basis functions which are related to the eigenfunctions of the hydrogen atom. We have studied the effect of adaptivity for different types of Daubechies wavelets. The comparatively large box size is rather typical for our applications. It reflects the multi-scale structure of the orbitals, i.e., in Hartree-Fock theory it is the energetically highest occupied orbital which determines the box size, whereas the orbital lowest in energy defines the finest resolution level. Furthermore, our large box size avoids boundary effects for Daubechies wavelets of high degree which have large supports. A finite level cut-off was introduced, i.e., the expansion of products of wavelets and scaling functions in (18) and (19) has been restricted to $l \leq n - 1$ where $n - 1$ is the finest level of the wavelet representation of the individual functions f and g . In order to judge the effect of adaptivity, we have counted the number of products in (22), using already contracted coefficients (23), which are greater than a certain threshold ϵ . Results are shown in Fig. 3 for D2 and D10 Daubechies wavelets. Apparently, the total number of products is much smaller in the case of D2 compared with D10. The higher degree of D10 is counterbalanced by the larger support and the huge number of additional products which arise from the wavelet expansion (19).

5 Computation of products of orbitals

In this section, we want to consider a realistic application of the non-standard algorithm for products of orbitals of the C_2H_6 molecule. The orbitals are conve-

niently represented in a Cartesian-Gaussian basis set (3) which is standard in quantum chemistry. Following our previous work [11,12], we have taken the best rank- κ approximation of orbitals in the canonical tensor product format, i.e.,

$$\Psi_a(\mathbf{x}) \approx \sum_{k=1}^{\kappa} \psi_{a,k}^{(1)}(x_1) \psi_{a,k}^{(2)}(x_2) \psi_{a,k}^{(3)}(x_3),$$

as a starting point for further calculations. The product of two orbitals is given as

$$\Psi_a(\mathbf{x})\Psi_b(\mathbf{x}) \approx \sum_{k,k'=1}^{\kappa} P_{ab,kk'}^{(1)}(x_1)P_{ab,kk'}^{(2)}(x_2)P_{ab,kk'}^{(3)}(x_3), \quad (25)$$

where univariate products

$$P_{ab,kk'}^{(i)}(x_i) = \psi_{a,k}^{(i)}(x_i) \psi_{b,k'}^{(i)}(x_i)$$

have been computed with the non-standard algorithm using precontracted coefficients (23). In Fig. 4, we present the computational complexity for the product of two valence orbitals Ψ_3, Ψ_4 lowest in energy of the C_2H_6 molecule using D2, D4, D6 and D10 Daubechies wavelets. The tensor rank $\kappa = 10$ was chosen and the underlying mesh contained $N = 5121$ grid points in each direction. A straightforward pointwise computation of the product on this grid requires $3N\kappa^2 = 1,536,300$ multiplications. This number can be reduced through the non-standard algorithm e.g., by a factor of 15 if we take $\epsilon = 10^{-3}$. It can be seen that the D4, D6 or D10 Daubechies wavelets require almost the same number of products. The advantage of a higher number of vanishing moments is obviously counterbalanced by the larger supports of the corresponding wavelets. Remarkably, for D2 wavelets the number of products can be reduced by a factor of 54 for the same ϵ .

6 Computation of two-electron integrals

In Hartree-Fock, hybrid density functional theory and post-Hartree-Fock methods, one needs to compute a huge number of two-electron integrals which goes along with a high computational complexity. The application of tensor product approximations to simplify the computation of two-electron integrals was our main motivation for the present work. It is therefore essential to test the performance of the non-standard algorithm for such integrals. In the following we consider exchange integrals

$$K_{ab} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \Psi_a(\mathbf{x})\Psi_b(\mathbf{x}) \frac{1}{|\mathbf{x} - \mathbf{y}|} \Psi_a(\mathbf{y})\Psi_b(\mathbf{y}) d\mathbf{x} d\mathbf{y}$$

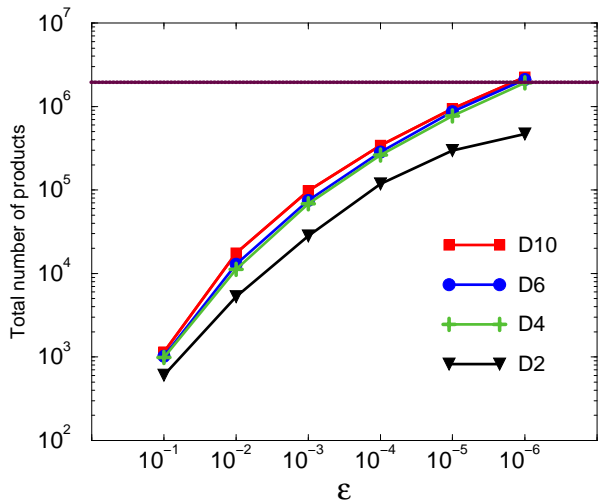


Fig. 4 Computational complexity of the non-standard algorithm with precontracted coefficients for the product of two valence orbitals of C_2H_6 for various Daubechies wavelets. The horizontal line indicates the number of multiplications required by a pointwise computation of the product on the finest grid.

for the C_2H_6 molecule. Integrals of this type appear in Hartree-Fock and hybrid density functional theory. The latter comprises a compromise between the purely non-local Hartree-Fock exchange and the local exchange potentials in standard density functional theory. Presently, the most accurate density functionals used in quantum chemistry are of this type, e.g., the popular B3LYP hybrid functional [43]. In order to deal with the Coulomb potential, it is convenient to use a tensor product approximation based on a quadrature formula for the integral representation

$$\begin{aligned} \frac{1}{|\mathbf{x} - \mathbf{y}|} &= \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-|\mathbf{x} - \mathbf{y}|^2 t^2} dt \\ &\approx \sum_{m=-M}^M w_m e^{-|\mathbf{x} - \mathbf{y}|^2 t_m^2}, \end{aligned}$$

c.f., [12] for further details. The computation of exchange integrals is performed in several steps. Once the product (25) has been computed, it is convenient to perform first a recompression step [11] in order to reduce the tensor rank of the product. This step introduces, however, an additional approximation error and therefore we refrained from doing it in the present work. The next step is the convolution of the orbital product with the Coulomb interaction in the tensor format

$$\begin{aligned} \int_{\mathbb{R}^3} \frac{1}{|\mathbf{x} - \mathbf{y}|} \psi_a(\mathbf{y}) \psi_b(\mathbf{y}) d\mathbf{y} &\approx \sum_{m=-M}^M \sum_{k,k'=1}^{\kappa} W_{ab,mkk'}^{(1)}(x_1) \\ &\times W_{ab,mkk'}^{(2)}(x_2) W_{ab,mkk'}^{(3)}(x_3), \end{aligned}$$

with

$$W_{ab,mkk'}^{(i)}(x_i) = w_m^{1/3} \int_{\mathbb{R}} e^{-|x_i - y_i|^2 t_m^2} P_{ab,kk'}^{(i)}(y_i) dy_i.$$

It remains to calculate the scalar product of the convolution with the orbital product, i.e.,

$$\begin{aligned} K_{ab} &\approx \sum_{m=-M}^M \sum_{k,k'=1}^{\kappa} \int_{\mathbb{R}} P_{ab,kk'}^{(1)}(x_1) W_{ab,mll'}^{(1)}(x_1) dx_1 \\ &\times \int_{\mathbb{R}} P_{ab,kk'}^{(2)}(x_2) W_{ab,mll'}^{(2)}(x_2) dx_2 \\ &\times \int_{\mathbb{R}} P_{ab,kk'}^{(3)}(x_3) W_{ab,mll'}^{(3)}(x_3) dx_3, \end{aligned}$$

which yields the final exchange integral.

In our test calculations, we considered different combinations of orbitals for the C_2H_6 molecule. The orbitals Ψ_1, Ψ_2 represent core orbitals which are dominated by the smallest length scales in our multi-scale wavelet bases. All other orbitals Ψ_3 to Ψ_9 are valence orbitals which mainly correspond to intermediate length scales. In Table 1, we have listed absolute errors of the non-standard algorithm without further truncation, i.e., $\epsilon = 0$, for D2, D4 and D10 Daubechies wavelets. For D2 the error is of the order of machine accuracy whereas for D4 and D10 substantially larger errors due to the finite level cut-off for the coupling coefficients has been observed. The errors for D4 and D10 are at most 10^{-6} a.u. and therefore acceptable for the Hartree-Fock model. In order to benefit from the non-standard algorithm, it is necessary to truncate the evaluation of products at a certain threshold ϵ . The effect of truncation on exchange integrals are listed in Table 2. It can be seen that the D2 wavelet outperforms D4 and D10 wavelets of higher degree which is a consequence of the exact representation of wavelet products. For wavelets of higher degree, the expansion of wavelet products gives rise to additional truncations which results in a larger approximation error.

Table 1 Accuracy of exchange integrals for C_2H_6 molecule using the non-standard algorithm for the computation of products of orbitals. Besides a level cut-off for the coupling coefficients no further truncation has been performed, i.e., $\epsilon = 0$. Absolute errors are given for D2, D4 and D10 Daubechies wavelets.

$\Psi_a \Psi_b$	$\Psi_1 \Psi_2$	$\Psi_1 \Psi_3$	$\Psi_3 \Psi_4$	$\Psi_4 \Psi_5$	$\Psi_5 \Psi_6$	$\Psi_6 \Psi_7$	$\Psi_7 \Psi_8$	$\Psi_8 \Psi_9$
K_{ab}	1.58	2.12E-2	1.14E-1	5.13E-2	1.94E-2	1.98E-2	2.00E-2	2.34E-2
Abs. error								
D2	2.00E-14	1.28E-16	9.99E-16	4.30E-16	1.80E-16	2.08E-16	1.91E-16	1.98E-16
D4	1.99E-07	8.88E-09	6.08E-09	2.42E-09	1.06E-08	1.07E-09	2.08E-09	1.75E-08
D10	2.34E-06	1.64E-06	7.28E-07	5.43E-09	1.23E-09	3.88E-10	2.04E-09	2.19E-09

Table 2 Effect of truncation for products of orbitals on exchange integrals of C_2H_6 molecule for D2, D4 and D10 Daubechies wavelets. Different values of the threshold ϵ are considered.

ϵ	1.0E-2	1.0E-3	1.0E-4	1.0E-5	1.0E-6
$\Psi_1 \Psi_2$					
D2	6.44E-02	2.94E-03	2.71E-05	2.11E-06	1.23E-07
D4	2.58E-01	4.36E-02	5.29E-04	2.41E-04	3.04E-05
D10	0.629796	1.05E-02	1.62E-03	2.33E-04	1.14E-05
$\Psi_1 \Psi_3$					
D2	1.32E-03	2.79E-05	2.04E-06	7.01E-08	3.73E-10
D4	4.09E-03	1.35E-03	9.78E-05	1.98E-06	6.21E-07
D10	1.49E-02	2.70E-04	4.97E-05	6.47E-06	1.47E-06
$\Psi_3 \Psi_4$					
D2	6.67E-03	1.69E-04	1.24E-05	4.14E-07	1.70E-08
D4	4.25E-03	1.57E-03	1.76E-05	1.60E-05	2.35E-06
D10	3.17E-03	3.85E-04	7.60E-05	1.04E-05	1.13E-06

7 Conclusions

We have studied a specific application of Beylkin's non-standard algorithm for the computation of products of orbitals, represented by wavelet bases, in quantum chemistry. The basic task is to find efficient algorithms for the computation of two-electron integrals which represents a bottleneck for many models in electronic structure calculations. We are presently studying a tensor product based approach for which the computation of products represents an essential step. The non-standard algorithm allows full exploitation of adaptivity which is of great significance for our envisaged applications in quantum chemistry. Different types of Daubechies wavelets have been considered for this purpose and it turned out that for our applications potential advantages of wavelets of higher degree are counterbalanced by their larger supports and an additional effort required for the expansion of wavelet products. This additional effort cannot be compensated by adaptivity. Furthermore, the finite level cut-off for coupling coefficients of higher degree wavelets introduces an additional approximation error which leads to larger thresholds for truncation in order to achieve a certain accuracy. It seems that simple D2 Haar wavelets are most suitable to compute products of orbitals in an efficient manner utilizing adaptivity and taking into account the multi-scale character of the problem under consideration. Finally, we want to mention that more complicated molecules, especially those including heavy elements, are much more challenging concerning adaptivity and for these molecules the real benefits of the non-standard algorithm should become even more visible.

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