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Canonical tensor products as a generalization of Gaussian-type orbitals

by

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We propose a possible generalization of Gaussian-type orbital (GTO) bases by means of canonical tensor products. The present work focus on the application of tensor product as an alternative to conventional GTO based density fitting schemes. Tensor product approximation leads to highly nonlinear optimization problems which require sophisticated algorithms. We give a brief description of the optimization problem and algorithm. The present work extends our previous paper [S. R. Chinnamsetty, M. Espig, B. N. Khoromskij, W. Hackbusch and H.-J. Flad, J. Chem. Phys. **127** (2007), 084110], where we discussed tensor product approximations of the electron density and the Hartree potential, to orbital products which are required for the exchange part of Hartree-Fock and in post Hartree-Fock methods. We provide a detailed error analysis for the Coulomb and exchange terms in Hartree-Fock calculations. Furthermore, a comparison is given between all-electron and pseudopotential calculations.

1. Introduction

In quantum chemistry, single-electron wavefunctions, the so-called orbitals, appear as solutions of various mean-field Schrödinger equations, e.g., Kohn-Sham or Hartree-Fock equations. Furthermore, these orbitals provide a natural starting point for the construction of Slater determinants which serve as a basis to represent many-electron wavefunctions which incorporate electron correlations. Since the early days of quantum chemistry, the optimal choice of basis functions for the approximation of orbitals has been a controversial issue which was finally decided by the majority of quantum chemists in favour of atomic centered *Gaussian-type orbital* (GTO) bases. Originally suggested by Boys [1], GTOs were first applied by Boys et al. [2] and Preuss [3] as basis sets for electronic structure calculations. From a physical point of view, GTOs seem to be only the second-best choice because they do not satisfy the required asymptotic properties close to a nucleus and at infinity. Compared with *Slater-type orbital* (STO) basis functions, which have the right asymptotic behaviour, GTOs, however, have the invaluable advantage of computational simplicity. This means that all the required integrals can be calculated analytically, cf., the monograph [4]. Furthermore it has been proven by Kutzelnigg and Braess [5,6] that the ground state of the hydrogen atom can be approximated with almost exponential,

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i.e., $O(e^{-c\sqrt{n}})$, convergence rate, by n GTO basis functions. Whether this result remains valid in the case of Hartree-Fock calculations for general molecules seems to be an open issue, although there exists some numerical evidence in favour of it, cf., Ref. [7].

Several well-known mathematical objections can be raised against GTO basis sets. These basis sets suffer from linear dependencies which means that they represent essentially over-complete bases so-called frames. As a consequence they are not stable in the sense of a Riesz basis [8] in our envisaged Hilbert spaces L^2 and H^1. These spaces consist of square integrable functions which in addition, in the case of the Sobolev space H^1, have square integrable first derivatives. However, everybody who tries to compete with GTOs using even the most sophisticated systematic basis functions, like wavelets [1], get puzzled from the almost unbelievable efficiency of GTOs at least for moderate accuracies. Although GTO bases are not a subject of standard approximation theory, their properties have been studied within *approximate approximation theory* [10]. Therein one has to give up the goal to turn GTOs into a systematic basis which can in principle achieve arbitrary accuracies. Instead it is advisable to content oneself with a certain residual error that enters in a controlled way into the construction of the basis set. This enables e.g., the construction of approximate multiscale bases similar to wavelets which provide a systematic error convergence rate up to a certain predetermined accuracy. Any attempt to turn GTOs into "systematic bases" is at the expense of loosing some flexibility which is actually a prominent feature of GTO bases. Therefore, the present work goes into a different direction. Instead of restricting flexibility, we seek to generalize GTOs by means of tensor product approximations of greatest possible generality.

GTOs are not only used for the expansion of orbitals but also for products of orbitals and electron densities. This requires the so-called auxiliary GTO basis sets which attracted considerable attention within *density fitting* schemes, also known as *resolution of the identity*, in order to reduce the computational complexity for Hartree-Fock and Kohn-Sham methods in particular for the Hartree potential [11–16] and also for two-electron integrals [17–22] in general. These techniques have been further applied to various post Hartree-Fock methods [23–28]. Related approaches are the Cholesky decomposition of two-electron integrals [29–31] and the pseudo-spectral method [32,33].

In the present work we want to consider possible generalizations of (auxiliary) GTO basis sets via tensor product approximations with "optimal" separation rank. Our approach does not restrict to orbitals, orbital products, and electron densities but can be also applied to their convolutions with the Coulomb potential, like for the Hartree potential. This means that we are looking for the best possible approximation of some function f in $\mathbb{R}^3$ in the canonical format

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

with $\mathbf{x} := (x_1, x_2, x_3)$, for fixed separation rank κ where the univariate functions $h_k^{(i)}(x_i)$, $k = 1, \ldots, \kappa$ for $i = 1, 2, 3$, so-called *Kronecker factors*, have to be chosen in an "optimal" manner. In particular, there are no orthogonality constraints imposed. Within the

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[1]The approximation of orbitals in wavelet bases has been studied in Ref. [9].

mathematical literature, such an approximation by a tensor product of a certain rank became known as *canonical decomposition* (CANDECOMP) or *parallel factors* (PARAFAC) model, cf., Ref. [34]. In the following we refer to κ as the Kronecker rank, a notion that has been borrowed from linear algebra [35] where it denotes the least possible decomposition rank of a tensor. We apply the more general notion of a separation rank to tensor product decompositions (1) for which the rank is supposed to be suboptimal, at least in some approximate manner.

Any function represented in a GTO basis can be considered as a tensor product in the format (1) where the possibly not optimal separation rank simply corresponds to the size of the basis set. In this sense, we consider tensor products as a generalization of GTO bases. It is the topic of the present work to study "optimal" tensor product approximations of such a function with fixed Kronecker rank κ which is much smaller than the size of the corresponding GTO basis set. Together with an appropriate tensor product approximation for the Coulomb potential this also enables fast convolutions in the tensor format which are required e.g., for the Hartree and exchange potentials. The tensor product format does not only provide separable representations for convolutions, moreover it offers the possibility to consider their further approximation with "optimal" separation rank. In this sense our approach goes beyond conventional GTO based density-fitting schemes.

The present work provides a general introduction into the subject where we present new results extending our previous work [36], hereafter denoted Paper I, which mainly focused on the Hartree potential. This paper is organized as follows: in Section 1.1 we give a concise overview on tensor product formats and related optimization problems. For illustrative purposes we first discuss some simple single-electron systems in Section 1.2 which is followed in Section 2 by tensor product approximations for individual orbitals. Next, we proceed in Section 2 to products of orbitals and the electron density. The latter, already discussed in Paper I, is positive everywhere and therefore easier to approximate than products between different orbitals which are required e.g., by the exchange potential and might have a rather complicated oscillatory behaviour near nuclei. In Section 2.1 we discuss our results using tensor product approximations to compute Hartree and exchange potentials for some small molecules. Although our focus is on the Hartree-Fock model, we want to mention that this approach can be easily extended to post Hartree-Fock methods similar to conventional GTO density-fitting schemes where already many successful applications have been reported in the literature. Finally we provide in Section 3 a comparison between all-electron and pseudo densities from calculations with pseudopotentials. This provides some insight how sensible tensor product approximations respond to electron-nuclear cusps.

1.1. Tensor product approximation

In the field of linear algebra, tensor products attracted considerable interest within the last few years [37,34]. A problem of general interest is to obtain an analogue for the *singular value decomposition* (SVD) of matrices for tensors of order > 2, cf., Ref. [38]. Here and in the following *order* denotes the number of Kronecker factors in each term of the tensor product. Within the present work we restrict to order three tensors. According to the Eckart-Young theorem, a SVD provides the best rank κ approximation of a matrix

by restriction to the largest κ singular values. There exits no canonical definition of a SVD analogue for tensors with order > 2 and various formats have been discussed in the literature [39–41]. The ultimate goal is to obtain best possible separable approximations of general tensors for a given separation rank. Furthermore, this task must be achieved with moderate computational effort and controlled accuracy. Most of the work has been done in a discrete setting which is equivalent to choosing a certain discretization for the Kronecker factors. In the following we give all of our expressions for functions. The reader should, however, keep in mind that for the actual computations these functions are represented on discrete grids, cf., Paper I for further details.

A popular alternative to the canonical format (1) is the Tucker format

$$f(\mathbf{x}) \approx \sum_{k_1,k_2,k_3=1}^{\varrho} b_{k_1,k_2,k_3} u_{k_1}^{(1)}(x_1)\, u_{k_2}^{(2)}(x_2)\, u_{k_3}^{(3)}(x_3), \tag{2}$$

where we can assume, without loss of generality, orthogonal Kronecker factors in each direction, i.e., $\langle u_{k_i}^{(i)}, u_{l_i}^{(i)} \rangle = \delta_{k_i,l_i}$, $k, l = 1, \ldots, \varrho$ for $i = 1, 2, 3$. The Tucker rank ϱ specifies the size of the core tensor $\mathbf{b} := \{b_{k_1,k_2,k_3}\}_{k_1,k_2,k_3=1,\ldots,\varrho} \in \mathbb{R}^{\varrho \times \varrho \times \varrho}$ with ϱ^3 entries. In the representation (2), the separation rank of the Tucker tensor product is ϱ^3, however, by a simple reordering we can obtain a canonical tensor product with separation rank ϱ^2. For the approximation of orbitals, orbital products and electron densities, the canonical and Tucker formats seem to be most appropriate [36,42,43]. Within the present work we restrict ourselves to the canonical format and refer to Ref. [43] for applications of the Tucker format to electronic structure calculations. Recently several new tensor formats [44–47] have been proposed in the literature which are especially of interest for higher order tensors. These formats might be of interest for post Hartree-Fock methods and density matrix theory. The usefulness of a tensor product format depends not only on its approximation properties but also on the possibility to apply differential or integral operators in this format in an efficient manner, cf., Refs. [48–51]. Furthermore, it is crucial to provide fast algorithms which compute the actual approximations (1) and (2) in the canonical format [52,53] and Tucker format [54–57], respectively.

The error of a best separable rank κ approximation is defined via the least-squares problem

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

where the error is measured in the L^2 norm, i.e., $\|f\|_{L^2}^2 := \int |f(\mathbf{x})|^2 d^3x$.

Our present algorithm for the least-squares problem (3) is based on Newton's method [52,53] and requires that the function f is already given in a tensor product format, i.e.,

$$f(\mathbf{x}) = \sum_{k=1}^{K} g_k^{(1)}(x_1)\, g_k^{(2)}(x_2)\, g_k^{(3)}(x_3), \tag{4}$$

like a linear combination of GTOs with initial separation rank K. It can be shown, cf., [41,52], that the optimal Kronecker factors $h_k^{(i)}$, $k = 1, \ldots, \kappa$, are contained in the subspace $U_i := \mathrm{span}\{g_k^{(i)}\}_{k=1,\ldots,K}$ for $i = 1, 2, 3$ which reduces the optimization problem to finite

dimension. The computational complexity of the various steps in the Newton algorithm is

$$\mathcal{O}\Big(\kappa(\kappa + K) + \kappa^3 + (\kappa + K)\sum_{i=1}^{3}\dim U_i\Big), \tag{5}$$

where $\kappa \ll K$ has been assumed, cf., Ref. [52,53]. In the worst case we have $\dim U_i = K$ which results in $\mathcal{O}(K^2)$ complexity for an orthogonalization step prior to the actual Newton optimization. However in our applications it turned out that often $\dim U_i \ll K$ after almost linear dependent functions have been removed from the set $\{g_k^{(i)}\}_{k=1,\dots,K}$.

The variational problem (3) is typically ill-posed, cf., Ref. [41], which means that a minimizer does not always exist. Nevertheless, it is possible to specify a set of functions $h_k^{(i)}(x_i)$ for which the error is arbitrarily close to σ_κ. However, it might happen that this set is ill-conditioned in a sense discussed in Ref. [53]. Another problem arises from a multitude of local minima into which a numerical algorithm for the solution of the variational problem (3) might get stuck. Despite these shortcomings, one should bear in mind that for our envisaged applications it is only of relevance to achieve a certain accuracy with a reasonably small Kronecker rank κ and it is completely irrelevant whether this representation actually corresponds to a global minimum.

The ultimate goal of the present work is to develop efficient schemes for the computation of two-electron integrals arising from localized occupied and virtual orbitals. This comprises applications to local correlation methods [58,59] and linear-scaling Kohn-Sham or Hartree-Fock methods [60] based on localized orbitals. In order to benefit from tensor formats, separable approximations of the Coulomb potential are required. These can be obtained from the familiar representation of the Coulomb potential via a Gaussian transform, we refer to Ref. [61] for further details. In Paper I, we have discussed a wavelet based approach for the canonical format which furthermore provides sparse approximations of the Kronecker factors. An alternative approach based on the Tucker format has been studied in Ref. [43]. Concerning our envisaged application, the L^2 norm underlying the least-squares problem (3) is not optimal. It is well known from various studies of density fitting schemes that the Coulomb norm gives considerably better results. We have argued in Paper I that the Coulomb norm is similar to the norm of the Sobolev space H^{-1}. It is work in progress to modify the Newton algorithm in order to allow for H^{-1} and various other norms.

1.2. Canonical tensor products versus GTOs

In order to judge the applicability of best separable rank κ approximations in quantum chemistry, we have studied orbital compression rates for a few single-electron systems. First we solved the Schrödinger equation using large uncontracted GTO basis sets. In the second step we have generated best separable rank κ approximations of the wavefunctions by minimizing the least-squares functional (3) and calculated the corresponding variational energy. The simplest single-electron system is the H atom. Errors in energy for best separable rank κ approximations obtained with the Newton algorithm are shown in Fig. 1 a). These have been compared with best radial Gaussian approximations of the same rank. The latter were optimized with respect to a weighted $L^\infty(\mathbb{R}_+)$ norm. It can be seen that both approaches lead to similar approximation errors, where the best
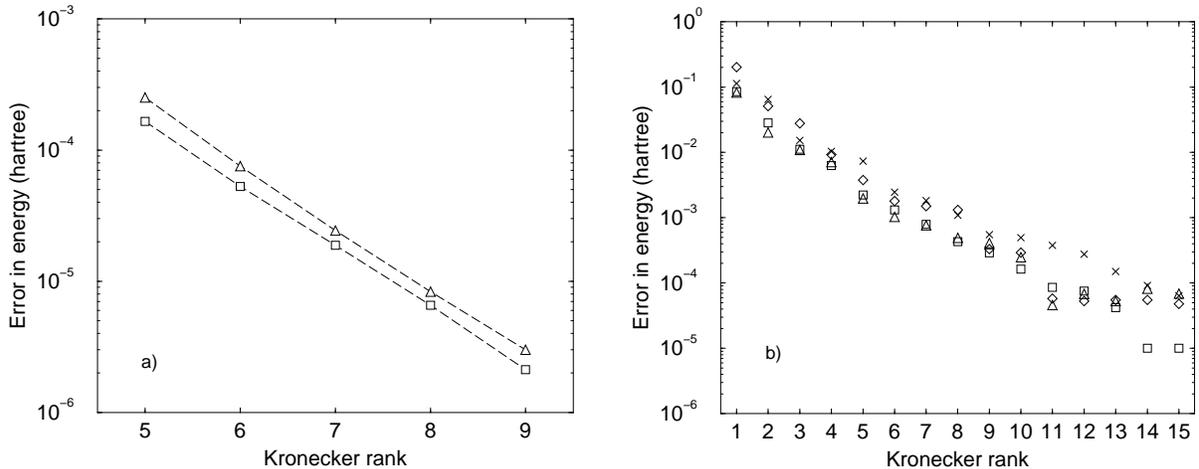
Figure 1.   Error in total energy (hartree) versus Kronecker rank κ of best separable approximations for one-electron wavefunctions. a) Best separable $L^2(\mathbb{R}^3)$ ($\square$) and best radial Gaussian $L^\infty(\mathbb{R}_+)$ ($\triangle$) approximations for the H atom. b) Best separable rank κ approximations for various positively charged dimers ($\square$) H_2^+ ($K = 58$), ($\diamond$) HHe^{2+} ($K = 58$), and trimers ($\triangle$) H_3^{2+} ($K = 126, \text{triangle}$), ($\times$) H_3^{2+} ($K = 75, \text{linear}$).

separable rank κ approximation performs only slightly better. Our results indicate that GTOs already provide almost optimal separable approximations for the H atom. However, this does not seem to be the case for systems with several nuclei as can be seen from Fig. 1 b) where significant compression rates have been achieved with respect to standard GTO basis sets. The exponents of the uncontracted $(8s4p3d)$ GTO basis were taken from V5Z basis sets [62]. Once the Schrödinger equation has been solved in this basis set, we compressed the wavefunctions for different Kronecker ranks $1 \leq \kappa \leq 15$. Thereafter, the set of rank-1 tensors $\{h_k^{(1)}(x_1)\, h_k^{(2)}(x_2)\, h_k^{(3)}(x_3)\}$ from the tensor product expansion (1) was taken as a new basis in which the Schrödinger equation was solved again. It should be mentioned that the approximation error of best separable rank κ approximations might depend on the orientation of the molecule with respect to the coordinate axes. The dimers H_2^+, HHe^{2+}, and a linear trimer H_3^{2+} were therefore oriented along the diagonal in order to avoid such kind of rank reductions due to symmetry. Furthermore, we have considered a triangular structure for H_3^{2+} with each nucleus located on an axis. The resulting errors in energy are shown in Fig. 1 b). It can be seen that the overall convergence for these systems is rather similar and an error in energy $\leq 10^{-4}$ hartree, which roughly corresponds to the basis set error of the GTO bases, can be achieved at Kronecker rank $\kappa \leq 15$. For comparison, the initial separation ranks of the GTO bases, ranging from $K = 58$ for H_2^+ up to $K = 126$ for H_3^{2+} (triangular structure), are considerably larger.

2. Orbitals and their products

The simple examples in the previous section illustrate that canonical tensor product approximations might be beneficial for molecular orbitals. An interesting question is how
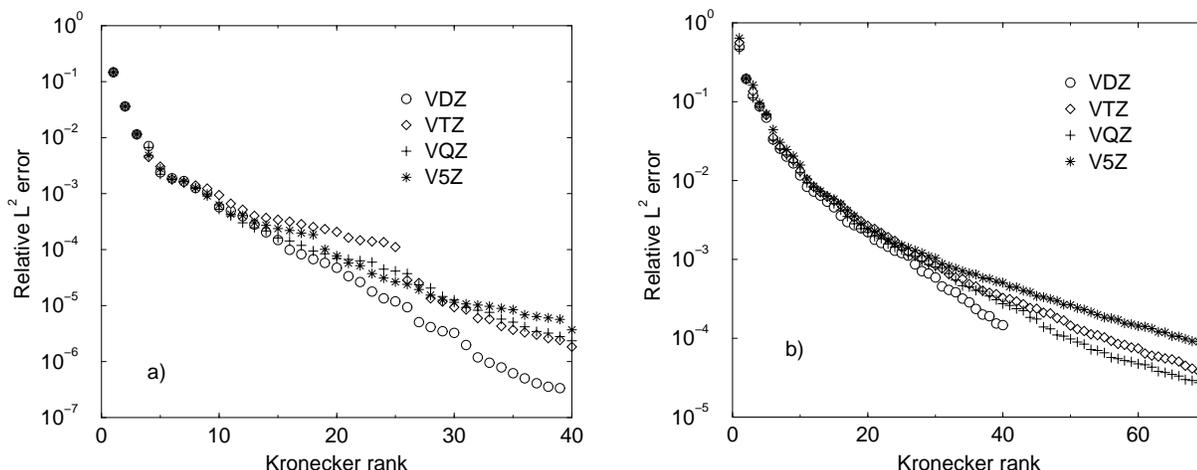
Figure 2. Relative L^2-error, i.e., $\sigma_\kappa(f)/\|f\|_{L^2}$ of tensor product approximations for orbitals represented by various GTO basis sets, ranging from VDZ up to V5Z. Results are shown for the core orbital (a) and the highest occupied orbital (b) of CH_4.

does the error for a certain Kronecker rank depend on the size of the GTO basis set. We have considered tensor product approximations for the orbitals of CH_4 represented in VDZ, VTZ, VQZ and V5Z basis sets. It can be seen from Fig. 2 that the approximation error for core and valence orbitals is not sensitive to the quality of the GTO basis set. However there is a marked difference between core and valence orbitals. The canonical tensor product approximation actually converges much faster for the $1s$ core orbital than for valence orbitals. It seems that the nuclear cusps do not restrain, at least in leading order, the convergence of the approximation. This is not surprising in view of the almost exponential convergence of GTO bases [5,6] mentioned before. Obviously, the spatially more extended valence orbitals with their richer structure require considerably higher Kronecker ranks in order to achieve a certain accuracy.

2.1. Density fitting via canonical tensor products

For our envisaged applications, canonical tensor product approximations of orbitals are of minor interest. Instead we are mainly interested in orbital products and the total electron density which appear in general two-electron integrals and the Hartree potential, respectively. Therefore our approach is closely related to conventional density fitting schemes based on auxiliary GTO basis sets. The pivotal question we have to answer is whether we can achieve a substantial reduction of the initial separation rank which might be worth the additional effort caused by the compression step. Presently, it seems to be premature to outline a detailed algorithm for a density fitting scheme based on canonical tensor products. However we can already highlight certain specific features of such a scheme.

(i) We expect our approach to be applicable to large molecules using localized orbitals. This is in agreement with the prevalent view adapted in local correlation methods [58,59] which are based on localized occupied and virtual orbitals. More recently,

linear-scaling Kohn-Sham and Hartree-Fock methods based on localized orbitals [60] have been studied.

(ii) Each tensor product approximation of a certain orbital product can be used many times in order to compute all the corresponding two electron integrals.

(iii) Further significant reductions of the separation rank can be achieved at the expense of the second compression step after the convolution of the orbital product with the Coulomb potential. This might be especially interesting for those orbital products which give contributions to a large number of two-electron integrals. We refer to Paper I where the compression of the Hartree potential has been studied in detail.

In Fig. 3, we have shown the relative L^2 errors of orbital products for the molecules CH_4, H_2O, C_2H_2, C_2H_6 and CH_3OH. The maximum errors for all molecules are of similar magnitude except for C_2H_2 where the maximal errors are considerably larger. A closer look reveals that the largest relative errors are from products between σ and π orbitals. It can be easily visualized that these products have the most complicated structures, however, their absolute values are comparatively small. Another significant difference can be observed for products where core orbitals contribute which have much smaller relative errors than the rest. This can be understood from our discussion of the compression of individual orbitals where core orbitals were shown to have much smaller errors for a given Kronecker rank than valence orbitals.

The canonical tensor product approximation for products of orbitals can be directly applied to compute the corresponding Coulomb and exchange contributions. Some results concerning the error of the Hartree-Fock energy for different Kronecker ranks are listed in Table 1. It can be seen that the absolute errors for $\kappa = 45$ are well below 1 mhartree, except for CH_3OH where a slightly larger Kronecker rank, i.e., $\kappa = 75$, is required. A more detailed analysis of the error has been shown in Fig. 4 for CH_3OH, where we have considered the Coulomb and exchange contributions of each orbital separately, i.e.,

$$\mathcal{J}_a := \sum_{b=1}^{N/2} (aa|bb), \quad \mathcal{K}_a := \sum_{b=1}^{N/2} (ab|ab). \tag{6}$$

Increasing the Kronecker rank from $\kappa = 45$ to $\kappa = 75$ reduces the error for most of the orbitals by an order of magnitude. It can be seen that the errors are roughly the same for all orbitals where the errors for the exchange part are smaller than for the Coulomb contribution.

3. Pseudopotentials

For standard GTO basis sets, a relatively small number of contracted primitive GTOs are sufficient for the representation of core orbitals. In our tensor terminology this means that they can be efficiently approximated by low rank tensor products. An alternative approach is to replace the core electrons by pseudopotentials. This has the further advantage that it also allows for smaller valence basis sets because for pseudo valence orbitals the orthogonality constraint with respect to the core orbitals must not be retained. We have studied the effects of pseudopotentials on the tensor product approximation of the
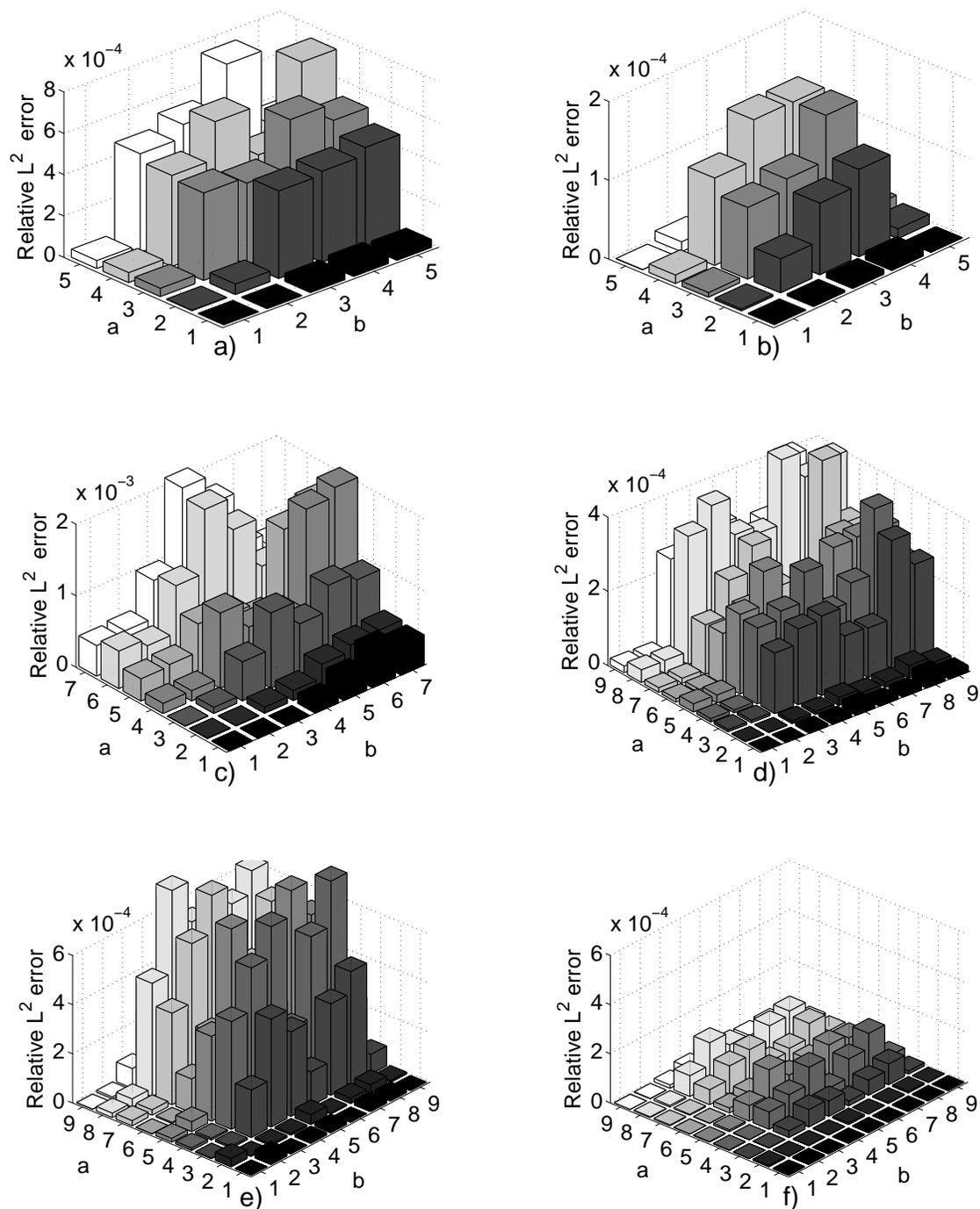
Figure 3. Relative L^2 error, i.e., $\sigma_\kappa(f)/\|f\|_{L^2}$ of canonical tensor product approximations of orbital products for the molecules CH_4 (a), H_2O (b), C_2H_2 (c), C_2H_6 (d) and CH_3OH (e,f). Results are shown for Kronecker rank $\kappa = 45$ (a-e) as well as $\kappa = 75$ (f) in the case of CH_3OH. All orbitals were originally represented in VDZ basis sets.
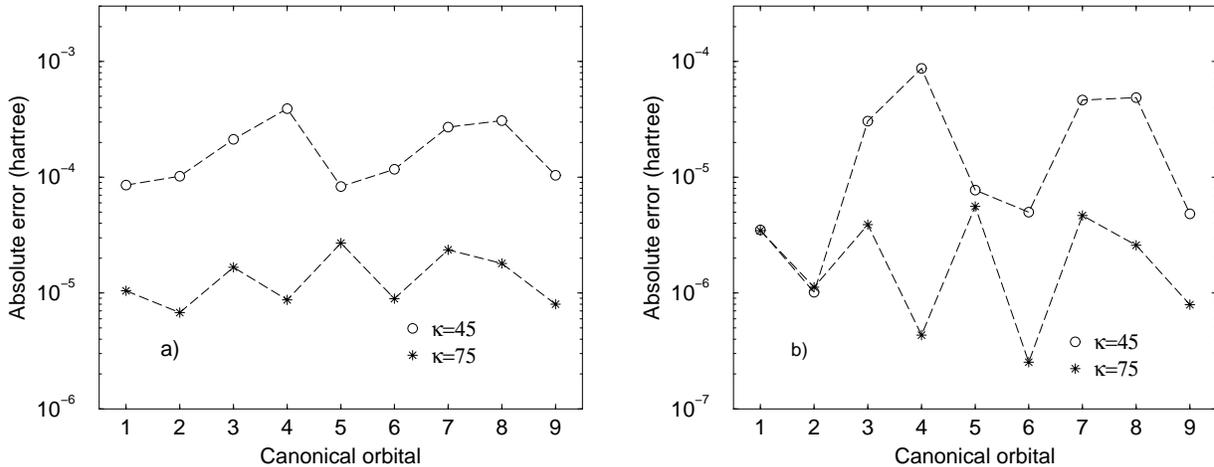
Figure 4. Individual contributions of the canonical orbitals of CH_3OH to the error of Coulomb (a) and exchange (b) energy, cf. (6), in the canonical tensor product density fitting scheme. Results are shown for Kronecker ranks $\kappa = 45$ and $\kappa = 75$.

Table 1
Error in the Hartree-Fock energy $E_{HF}^{GTO} - E_{HF}^{\kappa}$ (hartree) for different Kronecker ranks κ of the canonical tensor product density fitting scheme.

κ	H_2O	CH_4	C_2H_2	C_2H_6	CH_3OH
45	2.92×10^{-4}	7.26×10^{-4}	1.20×10^{-3}	1.05×10^{-3}	3.13×10^{-3}
55	1.64×10^{-4}	5.34×10^{-4}	6.45×10^{-4}	2.54×10^{-4}	1.18×10^{-3}
75	-	-	-	-	2.16×10^{-4}

electron density for the simple molecules CH_4 and SiH_4. Semilocal energy-consistent pseudopotentials [63] have been used for C and Si. These pseudopotentials still contain a singular Coulomb potential with respect to the effective charge of the atomic core. For Si, we have also tested a new type of smooth pseudopotential which has been developed especially for applications in quantum Monte Carlo calculations [64]. This pseudopotential has no singular term anymore and results in a smoother behaviour of the pseudo orbitals near nuclei.

In order to study the effect of pseudopotentials on canonical tensor product approximations, we considered only the total (pseudo) electron density instead of individual orbital products. The tensor product approximation was then used to calculate the Hartree potential according to the procedure described in Paper I. We have listed in Table 2 the error in the Hartree-Fock energy due to the density fitted Hartree potential for different Kronecker ranks. It can be seen that for CH_4 the errors for the pseudopotential and the all-electron calculation are almost the same. Going from CH_4 to SiH_4 increases the size of the core region however absolute errors up to $\kappa = 20$ are similar. At higher ranks the

Table 2
Error in the Hartree-Fock energy $E_{HF}^{GTO} - E_{HF}^{\kappa}$ (hartree) for different Kronecker ranks κ of the tensor product approximation of the (pseudo) electron density. Results are shown for all-electron (AE) and pseudopotential (PP) calculations.

	CH$_4$		SiH$_4$	
κ	PP^a	AE	PP^a	PP^b
15	1.92×10^{-3}	3.25×10^{-3}	-1.30×10^{-3}	-
20	6.64×10^{-4}	5.67×10^{-4}	5.17×10^{-4}	-1.23×10^{-3}
25	6.05×10^{-4}	5.41×10^{-4}	-9.23×10^{-5}	1.75×10^{-4}
30	1.38×10^{-4}	5.15×10^{-4}	1.98×10^{-5}	1.33×10^{-4}
35	1.00×10^{-4}	9.40×10^{-5}	2.37×10^{-5}	5.77×10^{-5}
40	8.70×10^{-5}	8.44×10^{-5}	1.55×10^{-5}	5.14×10^{-5}
45	3.89×10^{-5}	5.50×10^{-5}	1.39×10^{-5}	4.35×10^{-5}
50	4.62×10^{-5}	5.31×10^{-5}	5.91×10^{-6}	4.34×10^{-5}

[a] Energy consistent pseudopotentials from Ref. [63].
[b] Pseudopotential without singular term from Ref. [64].

errors for SiH$_4$ are on the average by a factor of 6 smaller. For comparison, the smooth pseudopotential has larger errors, varying between a factor of 2 to 7, than the standard pseudopotential. Our results indicate that tensor product approximations are not very sensitive with respect to nuclear cusps of the electron density.

4. Conclusions

We have studied an alternative to conventional GTO based density fitting schemes using canonical tensor product approximations for orbitals, products of orbitals and the electron density. It has been demonstrated that a considerable reduction of the initial separation rank with respect to GTO bases has been achieved, despite the fact that our optimization scheme uses the L^2 norm which is considered not to be optimal. The present work represents the first step into the largely unexplored landscape of tensor product approximations in quantum chemistry. Nevertheless, the highly successful GTO based density fitting schemes set high standards for all future work in this area. Taking into account the substantial computational effort to determine canonical tensor product approximations, it will require considerable efforts to develop a tensor product based density fitting scheme which becomes competitive to GTO auxiliary bases. It is our appraisement, however, that research in tensor product approximation is still at the very beginning and significant progress can be expected in the near future.

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