Max-Planck-Institut
für Mathematik
in den Naturwissenschaften
Leipzig

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by

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Preprint no.: 66 2008

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October 8, 2008

Abstract

The computational complexity of ab initio electronic structure methods can be decreased through the so-called density fitting scheme. The density fitting scheme is also known as resolution of identity (RI). Density fitting schemes became a popular approach to approximate the four-centre two-electron integrals which appear in the computation of the Fock matrix in the Hartree-Fock (HF) method. In the HF method, the computational effort to compute the Fock matrix scales with the fourth power of the number of basis functions, i.e., N_{BF}^4. Therefore, we need to compute a huge number of integrals for large molecules. This cost can be reduced by using density fitting schemes. In recent years, density fitting schemes became a popular approach not only in the HF method, but also in almost all post-HF methods, where the computation of the two-electron integrals provides a major bottleneck. Traditionally quantum chemists consider the tensor product approximation in terms of Gaussians. We propose a new look at the subject of density fitting from the point of view of optimal tensor product approximation to handle the two-electron integrals more efficiently. In order to improve the approximation quality near the nuclei, we apply the density fitting scheme for pseudo-potentials. Using pseudo-potentials not only improves the quality of approximation in the immediate neighbourhoods of the nuclei but also reduces the computational costs.

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

1 Density fitting schemes in electronic structure calculations

Gaussian-type orbital (GTO) basis functions are the most popular choice to deal with one- and two-electron integrals that appear in HF and post-HF methods, where the computation of the two-electron integrals

$$(\mu\nu|\sigma\lambda) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \phi_\mu^*(\mathbf{x})\phi_\nu(\mathbf{x})\frac{1}{\mid \mathbf{x}-\mathbf{y} \mid}\phi_\sigma^*(\mathbf{y})\phi_\lambda(\mathbf{y})\, d\mathbf{x}\, d\mathbf{y}, \text{ with } \mu,\nu,\sigma,\lambda \in \Delta, \qquad (1)$$

provides a major bottleneck for all conventional methods in quantum chemistry. As basis functions here are real, $\phi_\mu^*(\mathbf{x}) = \phi_\mu(\mathbf{x})$ holds. The products of two GTO basis functions are approximated in an auxiliary GTO basis set of larger size

$$\phi_\mu(\mathbf{x})\phi_\nu(\mathbf{x}) \approx \sum_{\alpha\in\Lambda} c_{\mu\nu,\alpha}\,\tilde{\phi}_\alpha(\mathbf{x}) \tag{2}$$

with $\#\Delta < \#\Lambda \ll \#\Delta(\#\Delta+1)/2$, where $\#\Delta$ is the size of the original GTO basis set and $\#\Lambda$ is the size of the auxiliary GTO basis set. The fitting GTO functions are termed as "auxiliary GTO basis functions". The coefficients $c_{\mu\nu,\alpha}$ are optimized with respect to the squared Coulomb norm

$$\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\Big(\phi_\mu(\mathbf{x})\phi_\nu(\mathbf{x}) - \sum_{\alpha\in\Lambda} c_{\mu\nu,\alpha}\tilde{\phi}_\alpha(\mathbf{x})\Big)\frac{1}{\mid \mathbf{x}-\mathbf{y} \mid}\Big(\phi_\mu(\mathbf{y})\phi_\nu(\mathbf{y}) - \sum_{\alpha\in\Lambda} c_{\mu\nu,\alpha}\tilde{\phi}_\alpha(\mathbf{y})\Big)d\mathbf{x}\,d\mathbf{y}, \tag{3}$$

which was found to be superior to the L^2-norm commonly employed for least-squares problems. The solution of the bilinear least-squares problem (3) leads to an expression for the approximation of four-centre integrals via three-centre integrals

$$(\mu\nu|\sigma\lambda) \approx \sum_{\alpha,\beta\in\Lambda} (\mu\nu|\alpha)(\alpha|\beta)^{-1}(\beta|\sigma\lambda), \tag{4}$$

where

$$(\mu\nu|\alpha) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \phi_\mu(\mathbf{x})\phi_\nu(\mathbf{x})\frac{1}{\mid \mathbf{x}-\mathbf{y} \mid}\phi_\alpha(\mathbf{y})\,d\mathbf{x}\,d\mathbf{y}. \tag{5}$$

This kind of approaches have been successfully applied not only to fit the Coulomb part [10, 11, 40] of the HF method, but also to fit the exchange part [12, 40] of it. HF algorithms using the resolution of identity (density fitting) for Coulomb and exchange integrals were studied and implemented by Früchtl et al. [12] and also by Weigend [40]. Using these approaches, the computational complexity of conventional HF method can be reduced.

Numerous successful applications [30, 1, 38, 10, 22, 23, 26] have been reported in quantum chemistry to reduce the computational effort in HF and Kohn-Sham (KS) equations, where the density is approximated in an auxiliary GTO basis. The density is required to compute the Hartree potential in HF and KS equations and it plays a major role concerning computational expenses. Approximation of the density $\rho(\mathbf{y})$ in an auxiliary GTO basis $\{\tilde{\phi}_\alpha,\ \alpha\in\Lambda\}$ yields

$$\rho(\mathbf{y}) = 2\sum_{b=1}^{N/2}\psi_b(\mathbf{y})\,\psi_b^*(\mathbf{y}) = \sum_{\mu,\nu\in\Delta}\rho_{\mu,\nu}\,\phi_\mu(\mathbf{y})\,\phi_\nu(\mathbf{y}) \approx \sum_{\alpha\in\Lambda}\varrho_\alpha\,\tilde{\phi}_\alpha(\mathbf{y}). \tag{6}$$

This method was originally introduced by Baerends, Ellis and Ros [2, 14] in density functional theory (DFT) for Slater-type orbital (STO) basis sets. Approximation of the density in auxiliary GTO basis has a great advantage in DFT.

Recently an interesting variant has been proposed by Manby and Knowles [22, 23], where basis functions with vanishing multipoles $\tilde{\phi}_\alpha := -1/4\pi\nabla^2\phi_\alpha$ have been considered. For such kind of basis functions the two- and three-centre Coulomb integrals reduce to simple overlap or kinetic energy integrals, i.e.,

$$\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\tilde{\phi}_\alpha(\mathbf{x})\,\frac{1}{\mid \mathbf{x}-\mathbf{y} \mid}\,\tilde{\phi}_\beta(\mathbf{y})\,d\mathbf{x}\,d\mathbf{y} = -\frac{1}{4\pi}\int_{\mathbb{R}^3}\phi_\alpha(\mathbf{x})\,\nabla^2\phi_\beta(\mathbf{x})\,d\mathbf{x}, \tag{7}$$

$$\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \tilde{\phi}_\alpha(\mathbf{x})\,\frac{1}{\mid \mathbf{x}-\mathbf{y} \mid}\,\phi_\sigma(\mathbf{y})\phi_\lambda(\mathbf{y})\,d\mathbf{x}\,d\mathbf{y} = -\frac{1}{4\pi}\int_{\mathbb{R}^3}\phi_\alpha(\mathbf{x})\phi_\sigma(\mathbf{x})\phi_\lambda(\mathbf{x})\,d\mathbf{x}. \tag{8}$$

This allows us to reduce the number of Coulomb integrals in density fitting by a factor around 10. In fact, most of the integrals are overlap integrals in this variant and these overlap integrals are much faster to evaluate than two-electron integrals (1).

Within the last few years density fitting methods became of widespread use in post-HF methods like second-order Møller-Plesset perturbation theory (MP2) [13, 3, 41, 42], coupled-cluster (CC) theory [29, 31] and r_{12}-methods [18, 24, 39] where individual orbital product densities $\rho_{ai}(\mathbf{x}) = \psi_a(\mathbf{x})\psi_i(\mathbf{x})$ have to be approximated instead of the total electron density (6). In MP2 theory, we need two-electron integrals $K_{ab}^{ij} = (ai|bj)$ with two occupied orbitals ψ_a, ψ_b and two virtual orbitals ψ_i, ψ_j [42]. These two-electron integrals K_{ab}^{ij} describe the electrostatic repulsion between two one-electron orbital product densities

$$K_{ab}^{ij} = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \rho_{ai}(\mathbf{x})\frac{1}{\mid \mathbf{x}-\mathbf{y} \mid}\rho_{bj}(\mathbf{y})\,d\mathbf{x}\,d\mathbf{y}, \tag{9}$$

where

$$\rho_{ai}(\mathbf{x}) = \psi_a(\mathbf{x})\psi_i(\mathbf{x}) \tag{10}$$

is one-electron orbital product density. Here orbitals are assumed to be real. The density fitting scheme applied to the second-order Møller-Plesset perturbation theory is denoted by RI-MP2 or density fitted MP2 (DF-MP2). In the DF-MP2 method, one-electron orbital product densities $\rho_{ai}(\mathbf{x})$ are approximated as in (6). Then four-centre two-electron integrals (9) are transformed to two- and three-centre integrals. Even if we apply the density fitting to MP2, the cost of this method scales with the fifth power of the number of basis functions, i.e., N_{BF}^5 as in the conventional MP2 method. Therefore the range of applicability of DF-MP2 is limited up to medium sized molecules. In order to overcome this limitation, Werner and his coworker [42] applied local approximations to remove the $O(N_{BF}^5)$ bottleneck in DF-MP2. This method is denoted as DF-LMP2.

The density fitting approaches were also used in CC theory for efficient computations with high accuracy. CC theory is considered to be one of the most successful models to deal with many-electron wavefunctions at high accuracy. The disadvantage of CC theory is an unfavourable scaling of the computational cost with the number of basis function N_{BF}. The computational cost of CC with single and double excitations (CCSD) scales as $O(N_{BF}^6)$. If the triple excitations are included, then the computational cost rises to $O(N_{BF}^7)$. By using the local correlation approach of Pulay and Saebø [27, 28, 34, 35], Hampel and Werner [16] and Schütz [32] achieved linear scaling for local CCSD (LCCSD) theory. Even for triple excitations in CC theory, linear scaling was obtained [33]. Later Schütz and Manby [31] applied the density fitting approach to deal with the most expensive class of two-electron integrals in LCCSD. In the context of density fitting approximation to LCCSD, locality was exploited for the fitting functions in order to achieve the linear scaling. It means that the range of fitting functions used to fit the one-electron orbital product density ρ_{ai} has to be confined to the spatial vicinity of ρ_{ai}. It was demonstrated by Schütz and Manby [31] that the approximate calculation of two-electron integrals via density fitting in LCCSD is 10-100 times faster than exact calculation via the $O(N_{BF})$ 4-index transformation in LCCSD.

The density fitting approaches were also successfully applied even in explicitly correlated [24] calculations. Highly accurate correlation energies can be obtained by introducing an explicit dependence on interelectronic distances into the wavefunction. Such kind of methods

are called explicitly correlated methods. These methods provide highly accurate energies and properties for light atoms and small molecules. But there are some difficulties for large systems due to computation of four-centre two-electron integrals in the explicitly correlated methods like MP2-R12. Manby [24] showed that density fitting applied to the explicitly correlated MP2 method, termed as DF-MP2-R12, requires only 2- and 3-centre integrals for Coulomb and exchange operators and is extremely efficient.

2 Density fitting with the best tensor rank κ approximations

We propose a new look at the subject of density fitting from the point of view of "optimal" tensor product approximations [4, 5]. The "optimal" tensor product approximation is performed in the sense that for a given accuracy an approximate tensor representation with minimal rank is determined. The rank of a tensor $\mathcal{A}$ is defined as the minimum number of products that are used to represent the tensor $\mathcal{A}$,

$$rank(\mathcal{A}) = min\Big\{\kappa \in \mathbb{N} : \mathcal{A} = \sum_{k=1}^{\kappa} v_k^{(1)} \otimes .... \otimes v_k^{(d)}\Big\}. \tag{11}$$

Tensor product decompositions with "optimal" rank provide an interesting alternative to traditional GTO basis functions. The basic idea behind the representation of certain quantities in terms of tensor products is to factorize expensive parts of the calculation. This reduces the dimensionality and thereby computational complexity. This is demonstrated for the evaluation of two-electron integrals.

Starting from a given tensor product in 3-dimension, i.e., a linear combination of GTOs, we obtain the best tensor rank κ approximations for densities of small molecules by using variations of the Newton method. We know that the product of two Gaussians is again a Gaussian. Using the Cartesian Gaussian representation of orbitals [4, 5] with coefficients c_k, the density of a molecule is given by

$$\rho(\mathbf{y}) = \sum_{k=1}^{K}\sum_{k'=1}^{K} c_k\, c_{k'}\, \rho_{kk'}^{(1)}(y_1)\, \rho_{kk'}^{(2)}(y_2)\, \rho_{kk'}^{(3)}(y_3), \tag{12}$$

where

$$\rho_{kk'}^{(i)}(y_i) = (y_i - A_k^{(i)})^{l_k^{(i)}} (y_i - A_{k'}^{(i)})^{l_{k'}^{(i)}} e^{-\frac{\alpha_k\alpha_{k'}}{\alpha_k+\alpha_{k'}}|A_k^{(i)}-A_{k'}^{(i)}|^2} e^{-(\alpha_k+\alpha_{k'})|y_i-A_{kk'}^{(i)}|^2} \text{ for } i = 1,2,3 \tag{13}$$

and

$$A_{kk'}^{(i)} = \tfrac{A_k^{(i)}\alpha_k + A_{k'}^{(i)}\alpha_{k'}}{\alpha_k+\alpha_{k'}} \text{ for } i = 1,2,3.$$

Here $A_k^{(i)}$ for $i = 1,2,3$ are the centres of the Gaussians, $l_k^{(i)}$ are the degrees of polynomials, c_k are the coefficients including normalization constants and α_k are the exponents of the Gaussians. It is our goal to obtain the best tensor rank κ approximations of the density $\rho(\mathbf{y})$. The initial rank of the density $\rho(\mathbf{y})$ is $K(K+1)/2$ due to symmetry. The best tensor rank κ approximation of the density is

$$\rho(\mathbf{y}) \approx \sum_{k=1}^{\kappa} \varrho_k^{(1)}(y_1)\, \varrho_k^{(2)}(y_2)\, \varrho_k^{(3)}(y_3), \quad \kappa \ll K(K+1)/2, \tag{14}$$

where $\varrho_k^{(1)}(y_1)$, $\varrho_k^{(2)}(y_2)$, and $\varrho_k^{(3)}(y_3)$ are the optimized one-dimensional components of the density $\rho(\mathbf{y})$ along the y_1-, y_2- and y_3-directions respectively. These optimized one-dimensional density components allow us to evaluate Coulomb integrals efficiently. The error of the approximations with fixed rank κ may be defined via

$$\sigma_\kappa(\rho) := \inf_{\varrho_k^{(i)} \in l^2(\mathbb{R})} \left\| \rho - \sum_{k=1}^{\kappa} \varrho_k^{(1)} \otimes \varrho_k^{(2)} \otimes \varrho_k^{(3)} \right\|_{l^2(\mathbb{R}^3)} \tag{15}$$

and is minimized with respect to the l^2-norm. More details have already been discussed in our previous article [4] and also in [5].

3 Density fitting for pseudo-potentials

It has been shown in our previous paper [4] that large errors in total electron density are located within the immediate neighbourhoods of the nuclei of atoms. These errors also propagate into the Hartree potential and finally into the HF energy. Various modifications to our approach seem to be possible in order to improve the approximation quality in the immediate neighbourhoods of nuclei. In this paper, we therefore study the density fitting for pseudo-potentials. The application of pseudo-potentials is also an obvious way to improve the efficiency. Using pseudo-potentials is a standard procedure to reduce the computational costs in electronic structure calculations and it becomes more important with increasing number of electrons. The basic idea of pseudo-potentials is to divide the electrons in an atom into two parts, i.e., core electrons and valence electrons. The core electrons remain essentially unchanged from the atom and provide the effective field for valence electrons [19]. The valence electrons participate strongly in interactions between atoms and are important for the calculation of many quantities. Therefore core electrons are assumed to be fixed and a pseudo-potential is constructed for each atomic species which takes the effect of nucleus and core electrons into account [19]. Therefore the use of pseudo-potentials reduces the many-electron problem to the valence electron problem. There are many different methods which have been proposed for the generation of pseudo-potentials [6, 17, 20, 7, 8, 15, 21]. The pseudo-potentials V($\mathbf{r}$) are of the form

$$V(\mathbf{r}) = -\frac{Q}{\mathbf{r}} + \sum_{l=0}^{l_{max}} \sum_{i=1}^{n} C_{li}\, exp(-\alpha_{li}\mathbf{r}^2) \cdot P_l, \tag{16}$$

where

$$P_l = \sum_{m=-l}^{+l} |Y_{l,m}\rangle\langle Y_{l,m}|. \tag{17}$$

Here Q is the core charge, P_l is the projector with the spherical harmonics $Y_{l,m}$ with angular momentum l, and n is the number of valence electrons. There is a slightly different approach the so-called model potentials [36, 37, 9]. For both pseudo-potentials and model potentials, core electrons are replaced by approximate potentials. Orbitals corresponding to the pseudo-potentials are the so-called pseudo-orbitals. Pseudo-potentials and associated pseudo-orbitals have been derived for many elements in such a way that the calculation of specific properties by using pseudo-potentials and pseudo-orbitals yields the same result as in the all-electron case. The pseudo-potential matches the true potential outside a given radius. Similarly,

the pseudo-orbital must match the corresponding true wavefunction beyond this distance. Pseudo-potentials are characterized by the number of core electrons and highest angular momentum l_{max} and corresponding pseudo-orbitals are then given by GTO basis functions. In order to improve the approximation quality in the immediate neighbourhood of nuclei, we study the possibility of applying pseudo-potentials. By using the pseudo-orbitals for CH_4, we obtain the reference pseudo-density and then the best tensor rank κ approximations of it.

Fig. 1 shows the reference pseudo-density on a plane passing through the C atom and two H atoms for CH_4. Relative L^2 errors of the best tensor rank κ approximations of the pseudo-density are presented in Fig. 2 and these relative L^2 errors are also compared with the relative L^2 errors of the best tensor rank κ approximations of the total electron density for CH_4. It can be seen from Fig. 2 that relative L^2 errors are almost the same for both cases. We present in Fig. 3 the absolute errors of the best tensor rank κ approximations of the pseudo-density. Here we plot the absolute errors of the best tensor rank κ approximations of the pseudo-density in a plane contain the C atom and two H atoms. As we can see from Fig. 3, the absolute error decreases very fast if we go to higher tensor ranks. It should be mentioned that the scale of our plots from Fig. 3 b) to Fig. 3 c) changes by an order of magnitude.

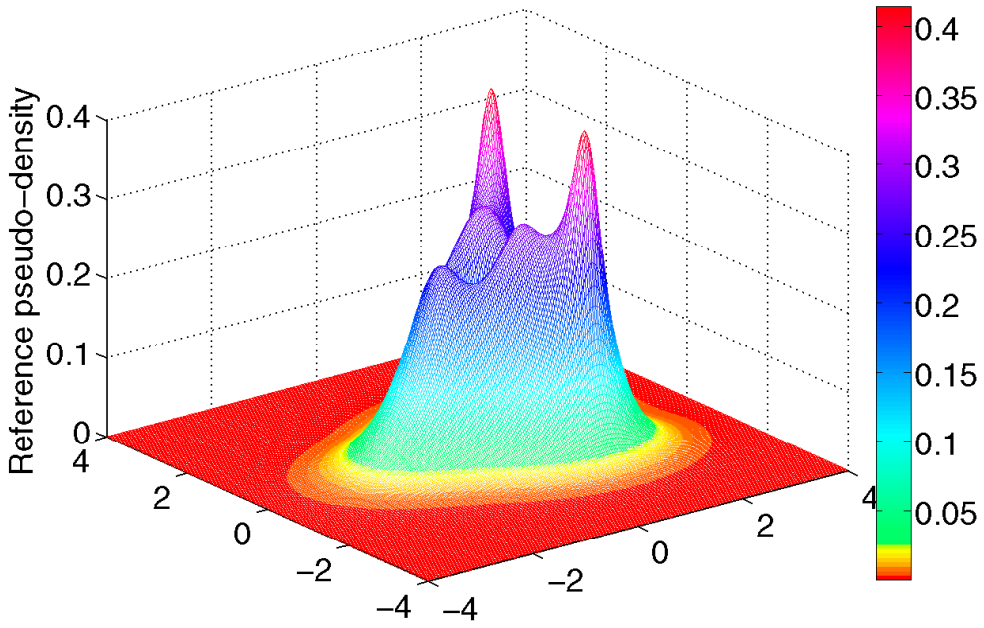

Figure 1: Reference pseudo-density on the plane passing through the C atom and two H atoms for CH_4 molecule.

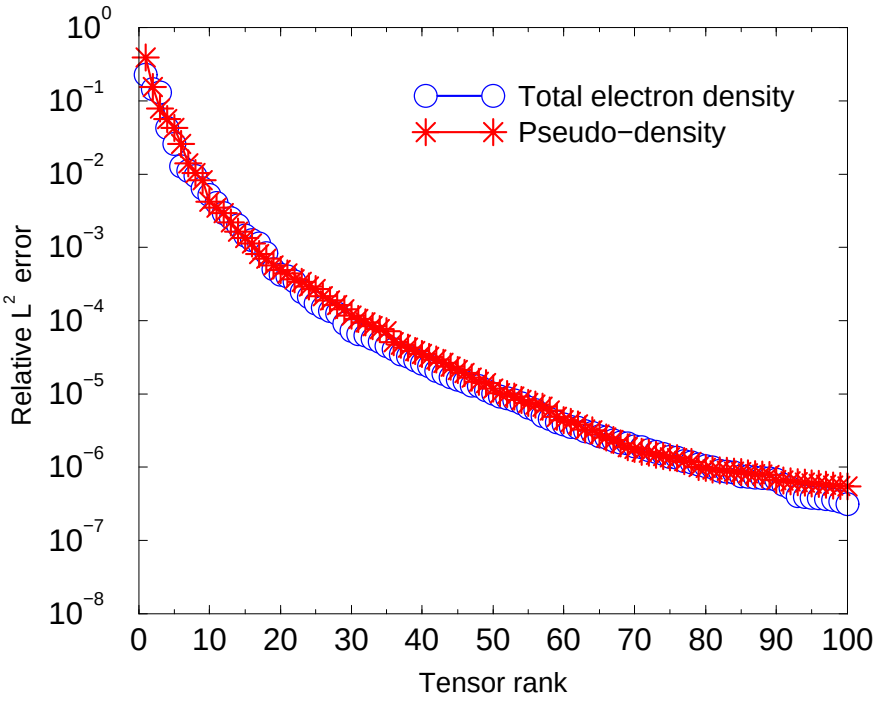

Figure 2: Relative L^2 errors of the best tensor rank κ approximations of the pseudo-density and the total electron density for CH_4.

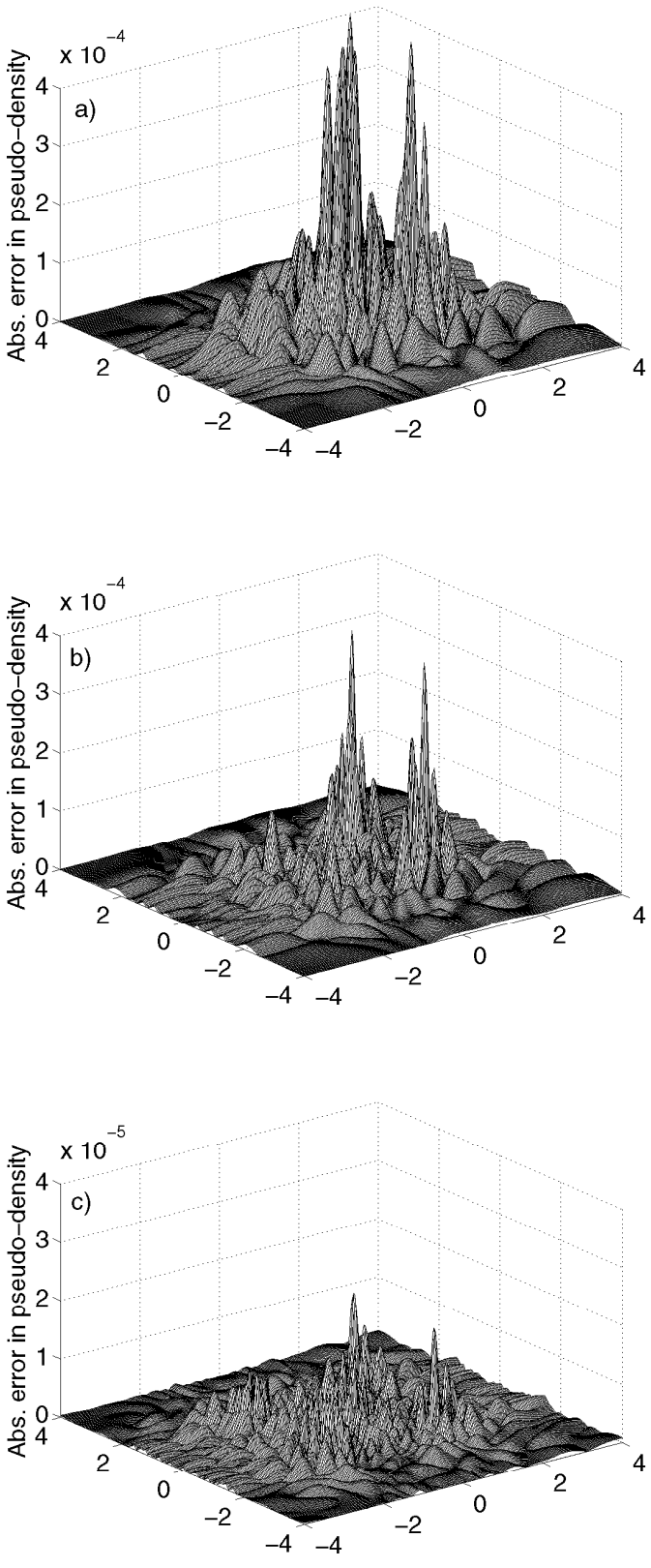

Figure 3: Absolute errors in the pseudo-density at best tensor rank a) $\kappa = 20$, b) $\kappa = 25$, c) $\kappa = 45$ approximations for CH_4 molecule.

4 Density fitting of the Hartree potential

The Hartree potential is one of the most complicated quantities in the Fock-operator and is a basic building block for the HF method and DFT. The Hartree potential plays an important role in computational expenses in electronic structure calculations and is given as

$$V_H(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{1}{|\mathbf{x}-\mathbf{y}|}\,\rho(\mathbf{y})\,d\mathbf{y}. \tag{18}$$

For an efficient treatment of the Hartree potential, we consider the tensor product representation of the Coulomb interaction and its convolution with the best tensor rank κ approximation of the density (14). The standard integration schemes for the evaluation of Coulomb integrals for GTO basis sets are based on the Gaussian transform of the Coulomb interaction

$$\frac{1}{|\mathbf{x}-\mathbf{y}|} = \frac{2}{\sqrt{\pi}}\int_0^\infty e^{-|\mathbf{x}-\mathbf{y}|^2t^2}dt \approx \sum_{m=-M}^{M} \omega_m\, e^{-|\mathbf{x}-\mathbf{y}|^2t_m^2}. \tag{19}$$

By using the Gaussian transform of the Coulomb interaction, we end up with

$$V_H^{DF}(\mathbf{x}) \approx \sum_{m=-M}^{M}\sum_{k=1}^{\kappa} V_{m,k}^{(1)}(x_1)\,V_{m,k}^{(2)}(x_2)\,V_{m,k}^{(3)}(x_3). \tag{20}$$

It represents the Hartree potential from the best tensor rank κ approximation of the pseudo-density and is called the pseudo-density fitted Hartree potential. It has the initial rank $(2M+1)\kappa$, where $(2M+1)$ is the total number of terms used to approximate the Coulomb interaction (19). It is more interesting from a practical point of view to take a look at the error distribution with respect to the Coulomb matrix elements. Therefore we compute the Coulomb matrix elements

$$J_{ab} = \int_{\mathbb{R}^3} g_a(\mathbf{x})\,V_H^{DF}(\mathbf{x})\,g_b(\mathbf{x})\,d\mathbf{x} \tag{21}$$

for all g_a and g_b of a GTO basis set.

5 Accuracy of the approximations

In Section 3, we have seen the best tensor rank κ approximation of the pseudo-density for CH_4. Now we see how errors in the pseudo-density propagate into the Hartree potential and then to the Coulomb matrix elements. For this, we first compute the reference Hartree potential (18) by using the GTO basis sets. We use the total electron density, valence density and pseudo-density to compute the reference Hartree potential (18). Fig. 4 shows the reference Hartree potential along the diagonal for the CH_4 molecule from the total, valence and pseudo-density. As we can see, there are two peaks at the origin where the C atom is located. The large peak corresponds to the Hartree potential from the total electron density. Small peaks correspond to the Hartree potential from the valence and pseudo-density. The Hartree potential from the pseudo-density is smoother even at the origin. The small picture in the right upper corner of Fig. 4 shows the tip of the Hartree potential from the valence density (red solid line) and from the pseudo-density (green dotted line).

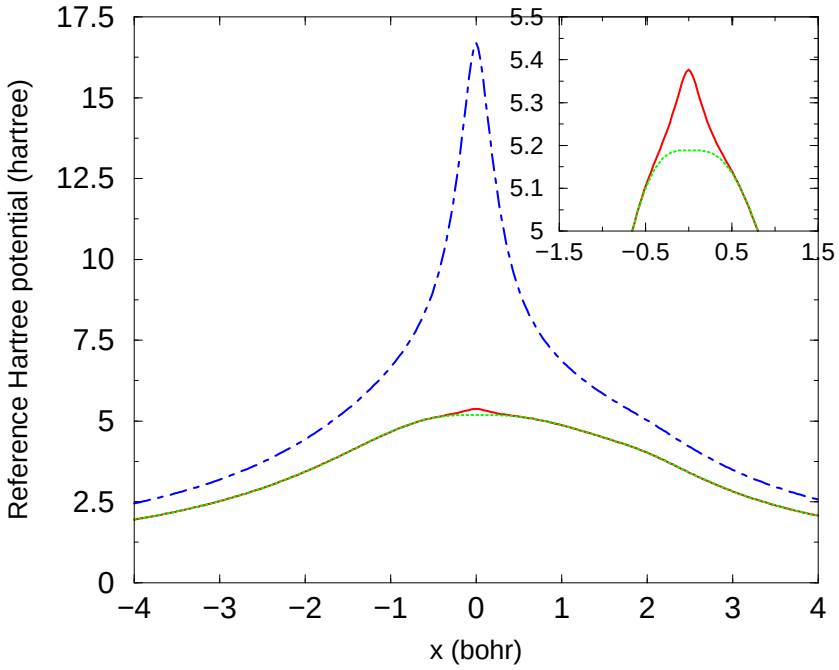

Figure 4: The reference Hartree potential $V_H(\mathbf{x})$ of CH_4 obtained from GTO basis set. The reference Hartree potential is computed from the total electron density (blue long dashed line), valence density (red solid line) and pseudo-density (green dotted line).

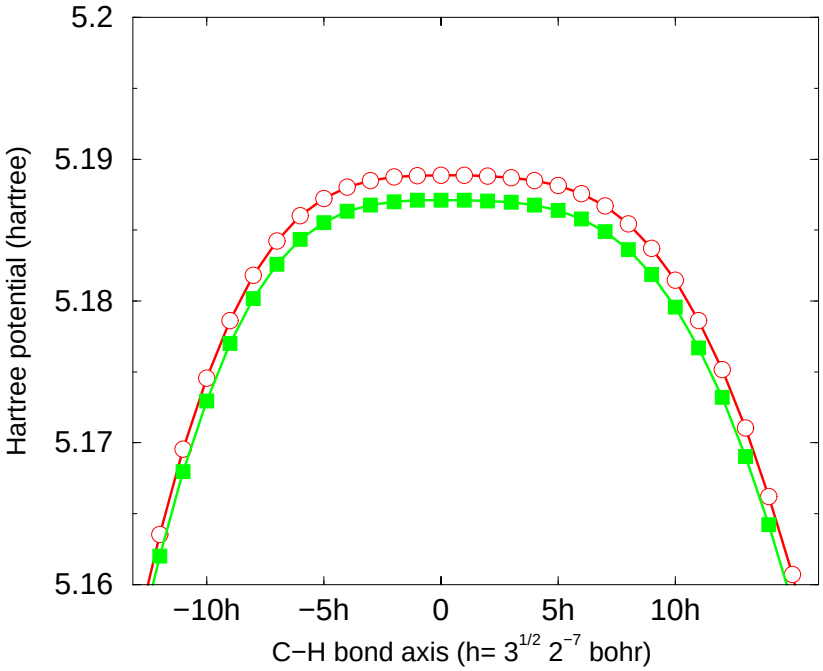

Figure 5: Pseudo-density fitted Hartree potential along the C-H bond axis for CH_4. The pseudo-density fitted Hartree potential (squares) is computed from the best tensor rank $\kappa = 10$ approximation of the pseudo-density. It is compared with the reference Hartree potential (circles).

Fig. 5 shows the pseudo-density fitted Hartree potential along the C-H bond axis near the C nucleus of CH_4. We use the best tensor rank $\kappa = 10$ approximation of the pseudo-density and $2M + 1$ quadrature points to compute the the Hartree potential and then compare with the reference pseudo-density. As we can see from Fig. 5, the Hartree potential from the pseudo-density is smoother even near the C nucleus of CH_4.

Fig. 6 shows the errors of Coulomb matrix elements J_{ab} corresponding to the pseudo-density fitted Hartree potential for CH_4 molecule. As we can see from Fig. 6 a) and Fig. 6 b), errors are uniformly distributed with the slightly larger peaks along the diagonal. This is due to the large exponents of Gaussians along the diagonal. Even though these peaks seem to be rather large their effect on the HF energy is fairly small.

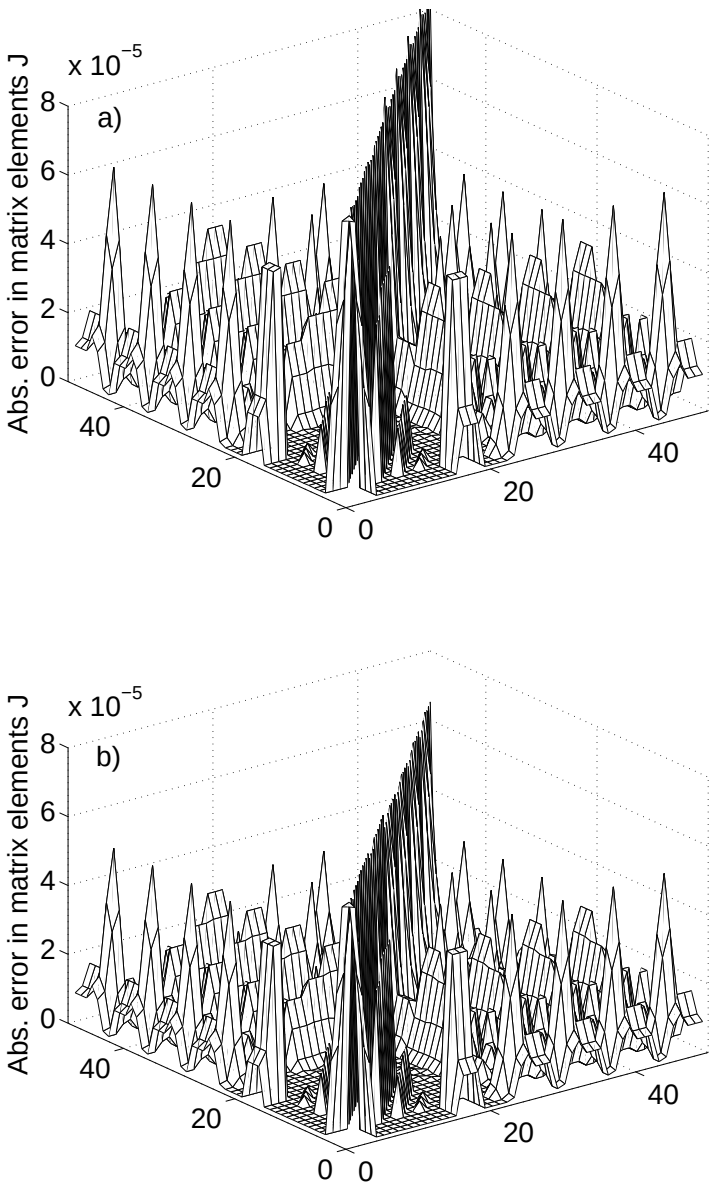

Figure 6: Errors of Coulomb matrix elements J_{ab} corresponding to the pseudo-density fitted Hartree potential at best tensor rank a) $\kappa = 20$, and b) $\kappa = 25$ for CH_4 molecule.

6 Hartree-Fock energy

To compute the Hartree-Fock energy corresponding to the pseudo-density fitted Hartree potential, we choose a slightly simplified approach in order to avoid multiple compressions of the pseudo-density within the iterative solution of the HF equation. We take the best tensor rank κ approximations from already self-consistent pseudo-density and then compute the Hartree potential (20) and corresponding Coulomb matrix elements (21) in a GTO basis set. In the HF calculation, the Coulomb part of the Fock matrix is kept fixed and only the exchange part is treated in a self-consistent manner. The HF calculations are carried out with the MOLPRO program package [25] using the MATROP program for matrix operations.

As discussed in Section 3, using pseudo-potentials not only decreases the computational costs but also improves the quality of approximation near the nuclei. It is useful in most cases because only the valence electrons determine many chemical properties such as bond strengths, electron affinities and ionization potentials. Orbitals corresponding to the pseudo-potential are the so-called pseudo-orbitals and orbitals corresponding to the model potentials [36, 37, 9] are nearly same as valence orbitals. In the case of pseudo-potentials, the pseudo-orbitals are not matched to the all-electron orbitals in the core region, i.e., the region below the cut-off radius r_c whereas the corresponding orbitals of the model potentials are matched to the all-electron orbitals even in the core region.

In the present work, we use only pseudo-potentials for electronic structure calculations because they are more appropriate for our approach. By using the pseudo-orbitals, we compute the best tensor rank κ approximation of the pseudo-density (14) and corresponding Hartree potential (20) and Coulomb matrix elements (21). We then perform SCF iterations and obtain the HF energy. Table 1 shows the HF energy and its error obtained from the pseudo-density fitted Hartree potential for CH_4 molecule. The absolute error in the HF energy for CH_4, obtained from the best tensor rank $\kappa = 45$ approximation of the pseudo-density is 3.9×10^{-5} hartree. This is roughly 1.5 times smaller than the absolute error of HF energy corresponding to the best tensor rank approximation of the total electron density at the same tensor rank, cf. [4]. We could not gain much from pseudo-potentials because relative L^2 errors of the best tensor rank κ approximations of the pseudo-density are almost the same as those in the case of the total electron density, as shown in Fig. 2. We also compute the HF energy from the pseudo-density fitted Hartree potential for the SiH_4 molecule. The HF energy and its error obtained from the pseudo-density fitted Hartree potential for the SiH_4 molecule are presented in Table 2. As we can see from Table 1 and Table 2, the accuracy of the HF energy obtained from the pseudo-density increases as tensor rank increases.

Table 1: HF energy and absolute error in the HF energy obtained from the pseudo-density fitted Hartree potential for CH_4 molecule. The original HF energy obtained from pseudo-potentials is -7.84226746 hartree.

Tensor rank κ	HF energy of CH_4 (hartree)	Error in HF energy (hartree)
10	-7.85096218	8.6947×10^{-3}
15	-7.84418853	1.9211×10^{-3}
20	-7.84293113	6.6367×10^{-4}
25	-7.84287270	6.0524×10^{-4}
30	-7.84240592	1.3846×10^{-4}
35	-7.84236794	1.0048×10^{-4}
40	-7.84235443	8.6970×10^{-5}
45	-7.84230634	3.8880×10^{-5}
50	-7.84231368	4.6220×10^{-5}
55	-7.84230847	4.1010×10^{-5}
60	-7.84230634	3.8880×10^{-5}

Table 2: HF energy and absolute error in the HF energy obtained from the pseudo-density fitted Hartree potential for SiH_4 molecule. The original HF energy obtained from pseudo-potentials is -6.07679941 hartree.

Tensor rank κ	HF energy of SiH_4 (hartree)	Error in HF energy (hartree)
10	-6.08820559	1.141×10^{-2}
15	-6.07549743	1.302×10^{-3}
20	-6.07731587	5.165×10^{-4}
25	-6.07670708	9.233×10^{-5}
30	-6.07681921	1.980×10^{-5}
35	-6.07682314	2.373×10^{-5}
40	-6.07681491	1.550×10^{-5}
45	-6.07681329	1.388×10^{-5}
50	-6.07680532	5.910×10^{-6}
55	-6.07679322	6.190×10^{-6}
60	-6.07679656	2.850×10^{-6}

7 Acknowledgments

The authors gratefully acknowledge Prof. Dr. Reinhold Schneider (Technische Universität Berlin) as well as PD Dr. Boris Khoromskij and Mike Espig (Max-Planck-Institut für Mathematik in den Naturwissenschaften, Leipzig) for useful discussions. This work was supported by the Deutsche Forschungsgemeinschaft (SPP 1145).

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