Institut für Numerische Simulation
Rheinische Friedrich-Wilhelms-Universität Bonn
Wegelerstraße 6 • 53115 Bonn • Germany
phone +49 228 73-3427 • fax +49 228 73-7527
www.ins.uni-bonn.de

M. Griebel, J. Hamaekers

Tensor Product Multiscale Many-Particle Spaces with Finite-Order Weights for the Electronic Schrödinger Equation

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Abstract

In this article we combine the favorable properties of efficient Gaussian type orbitals basis sets, which are applied with good success in conventional electronic structure methods, and tensor product multiscale bases, which provide guaranteed convergence rates and allow for adaptive resolution. To this end, we develop and study a new approach for the treatment of the electronic Schrödinger equation based on a modified adaptive sparse grid technique and a certain particle-wise decomposition with respect to one-particle functions obtained by a nonlinear rank-1 approximation. Here, we employ a multiscale Gaussian frame for the sparse grid spaces and we use Gaussian type orbitals to represent the rank-1 approximation. With this approach we are able to treat small atoms and molecules with up to six electrons.

1 Introduction

For many problems in quantum chemistry it is sufficient to consider nuclei as classical point-like particles and to only treat the electrons as quantum-mechanical particles. Then, the Born-Oppenheimer approximation of the time-dependent Schrödinger equation leads to a stationary electronic Schrödinger equation

$$H\Psi = E\Psi$$

with the spin independent molecular Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N}\Delta_i - \sum_{k=1}^{N_{\text{nuc}}}\sum_{i=1}^{N}\frac{Z_k}{|\mathbf{x}_i - \mathbf{R}_k|} + \sum_{i<j}^{N}\frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} + \sum_{k<l}^{N_{\text{nuc}}}\frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|}$$

written in atomic units. Here, N_{nuc} denotes the number of clamped nuclei $(\mathbf{R}_k, Z_k)$ and N is the number of electrons with coordinates $(\mathbf{x}_i)$. The solution of this N-electron problem lives in a $3N$-dimensional space and respects the antisymmetry condition imposed by Pauli's principle.

The high dimensionality of this eigenvalue problem turns out to be the main bottleneck for a direct numerical treatment, since any discretization on e.g. uniform grids with $\mathcal{O}(m)$ points in each direction would involve $M = \mathcal{O}(m^{3N})$ degrees of freedoms. Furthermore, only a convergence estimate of type

$$\|\Psi - \Psi_M\|_{\mathcal{H}^s} \leq c(N)M^{-r/(3N)}\|\Psi\|_{\mathcal{H}^{r+s}}$$

can be achieved, where $\|\cdot\|_{\mathcal{H}^s}$ is the usual Sobolev norm in $\mathcal{H}^s$, $r+s$ denotes the isotropic smoothness of Ψ and c is a constant which may depend on N but not on M. Here, we encounter the curse of dimensionality, i.e. the rate of convergence deteriorates exponentially with the number N of electrons. Therefore, further model approximations were developed and implemented in quantum chemistry which lead to reduced complexity. Examples are Hartree-Fock or multi-configuration methods (HF/MCHF) and a variety of additive methods (configuration interaction), exponential methods (coupled cluster), perturbative methods (Möller-Plesset theory), quantum Monte Carlo methods (VMC/DMC) and density functional theory methods (DFT). These *first principles* electronic structure methods are used with great success in practice. However, it is not yet completely clear how to systematically improve their approximation error in a mathematically rigorous way.

On the other hand, sparse grid techniques are frequently used to treat high dimensional problems. Sparse grids spaces are multiscale approximation spaces based on tensor products which promise to circumvent the above-mentioned curse of dimensionality of a conventional discretization using full grids, at least to some extent. We envision, up to logarithmic terms, a convergence estimate of the type

$$\|\Psi - \Psi_M\|_{\mathcal{H}^s} \leq c(N)M^{-r/3}\|\Psi\|_{\mathcal{H}^{r,s}_{\text{mix}}}, \tag{1}$$

where the rate of convergence does no longer exponentially deteriorate with the number N of particles. Note however, that a more restrictive smoothness requirement, namely the boundedness of a certain (r, s)-th mixed derivative is involved. In [1], Yserentant showed that the solution of the Schrödinger equation lies in certain spaces of mixed dominating smoothness, i.e. $\Psi \in \mathcal{H}_{\text{mix}}^{1/2,1}$, when the physically relevant antisymmetry of the wave function is taken into account. These spaces are closely related to the smoothness assumption of the conventional sparse grid method.

A first application of the sparse grid combination technique to the Schrödinger equation was studied in [2]. Furthermore, sparse grid approaches using Fourier basis functions and Meyer basis functions were implemented and studied in [3] and [4], respectively. Here, it turned out that, in principle, the sparse grid approach indeed possesses favourable approximation rates and cost complexities for the solution of Schrödinger's equation. However, the computations are limited due to large constants involved in the approximation rates and cost complexities. Actually, these constants can be exponentially dependent on the number of particles. Also in the framework of the variational Monte Carlo (VMC) approach wavelets and sparse grids have been successfully applied for the representation of Jastrow factors [5, 6].

In this article we propose a new approach for the electronic Schrödinger equation based on the combination of a nonlinear low-rank approximation method and sparse grid bases which provide guaranteed approximation rates. This combination is realized with help of a general particle-wise subspace splitting of the many-particle space which builds on so-called weighted spaces of finite order $q \ll N$. Then it is only the lower dimensionality of the q-th order terms, which exponentially enters the work count complexity for multilinear approximation problems [7–9]. In this way, we implement tensor product multiscale many-particle spaces with finite-order weights which are built from non-orthogonal Hartree-Fock orbitals and a variant of sparse grid spaces for many-particle functions. Here, to obtain favorably small constants, we present a multiscale frame of Gaussians and develop a heuristic h-adaptive refinement scheme for the resolution of cusps.

The remainder of this article is organized as follows: In Section 2 we recall the Pauli principle and many-particle Sobolev spaces of dominating mixed smoothness. Furthermore, we discuss the discretization with general sparse grid spaces and give estimates for approximation rates for electronic wave functions. In Section 3 we introduce weighted many-particle spaces based on a particle-wise subspace splitting and discuss our numerical approach for the solution of the electronic Schrödinger equation. Here, we introduce a multiscale Gaussian frame and describe our adaptive scheme. In Section 4 we present the results of our numerical experiments. Finally, some concluding remarks are given in Section 5.

2 Pauli principle, regularity of the wave function and general sparse grid spaces

In general, an electronic wave function depends on the positions $\mathbf{x}_i$ of the electrons and on their associated spin coordinates $s_i \in \{+\frac{1}{2}, -\frac{1}{2}\}$. It furthermore has to obey the antisymmetry conditions

$$\Psi(P\vec{\mathbf{x}}, P\vec{s}) = (-1)^{|P|}\Psi(\vec{\mathbf{x}}, \vec{s}), \quad \forall P \in \mathcal{S}_N,$$

which reflect the Pauli principle. Here, $\mathcal{S}_N$ denotes the symmetric group. Note that for a given spin distribution $\vec{s}$ the spatial part $\Psi_{\vec{s}}(\vec{\mathbf{x}}) := \Psi(\vec{\mathbf{x}}, \vec{s})$ obeys the partial antisymmetry condition

$$\Psi_{\vec{s}}(P\vec{\mathbf{x}}) = (-1)^{|P|}\Psi_{\vec{s}}(P\vec{\mathbf{x}}), \quad \forall P \in \mathcal{S}_{\vec{s}} := \{P \in \mathcal{S}_N \,:\, P\vec{s} = \vec{s}\}\,.$$

In particular, the minimal eigenvalue of all eigenvalue problems for the spatial components is equal to the minimal eigenvalue of the full eigenvalue problem [10, 11].

Although there are 2^N possible different spin distributions $\vec{s}$, the bilinear form $\langle\Psi(P\cdot)|H|\Psi(P\cdot)\rangle$ is invariant under all permutations $P \in \mathcal{S}_N$ of the position coordinates $\vec{\mathbf{x}}$. Thus, it is sufficient to consider $N+1$ eigenvalue problems which are associated with $N+1$ different class representative spin vectors with a total spin projection of values $M_S = -\frac{N}{2}, \ldots, -1, 0, 1, \ldots, \frac{N}{2}$ for even N and a total spin projection of values $M_S = -\frac{N}{2}, \ldots, -\frac{1}{2}, \frac{1}{2}, \ldots, \frac{N}{2}$ for odd N. Here, we choose the $N+1$ different class representative spin vectors $\vec{s}^{(M_S)} \in \{+\frac{1}{2}, -\frac{1}{2}\}^N$, where

$$s_j^{(M_S)} := \begin{cases} +\frac{1}{2} & \text{for } j \leq \frac{N}{2} + M_S, \\ -\frac{1}{2} & \text{for } j > \frac{N}{2} + M_S. \end{cases}$$

In the following we denote the number of spin-up particles by $N_\uparrow$ and the number of spin-down particles by $N_\downarrow$. Then $M_S = \frac{1}{2}(N_\uparrow - N_\downarrow)$. The functions of the N-particle space $\mathcal{L}^2((\mathbb{R}^3)^N)$ which obey the partial antisymmetry condition for a given $\vec{s}^{(M_S)}$ form a linear subspace $\mathcal{L}^2_{(M_S)} \subset \mathcal{L}^2$. We define the projection into this subspace, i.e. the antisymmetrization operator $\mathfrak{A}^{(M_S)} : \mathcal{L}^2((\mathbb{R}^3)^N) \to \mathcal{L}^2_{(M_S)}((\mathbb{R}^3)^N)$ by

$$\mathfrak{A}^{(M_S)}\Psi(\vec{\mathbf{x}}) := \frac{1}{N_\uparrow! N_\downarrow!} \sum_{P \in \mathcal{S}_{\vec{s}^{(M_S)}}} (-1)^{|P|}\Psi(P\vec{\mathbf{x}}).$$

The spatial part with respect to M_S of an electronic wave function is at least in $\mathcal{H}^1 \cap \mathcal{L}^2_{(M_S)}$. Let us assume that the smallest energy with respect to M_S, i.e.

$$E_{\min}^{(M_S)} = \min_{\Psi \in \mathcal{H}^1 \cap \mathcal{L}^2_{(M_S)}, \|\Psi\|_{\mathcal{L}^2}=1} \langle \Psi \,,\, H\Psi \rangle_{\mathcal{L}^2},$$

exhibits multiplicity one. Furthermore, let $\{V_\kappa\}_{\kappa\in\mathbb{N}}$ be an arbitrary dense family of finite-dimensional subspaces in $\mathcal{H}^1 \cap \mathcal{L}^2_{(M_S)}$. Let finally E_κ and Ψ_κ denote Galerkin approximations associated with the lowest state in the subspace V_κ, i.e.

$$E_\kappa = \min_{\Psi\in V_\kappa, \|\Psi\|_{\mathcal{L}^2}=1} \langle \Psi \, , \, H\Psi\rangle_{\mathcal{L}^2}, \quad \Psi_\kappa = \operatorname{argmin}_{\Psi\in V_\kappa, \|\Psi\|_{\mathcal{L}^2}=1} \langle \Psi \, , \, H\Psi\rangle_{\mathcal{L}^2}.$$

Then, $E^{(M_S)}_{\min} \leq E_\kappa$ for all $\kappa \in \mathbb{N}$ and thereby a relation between an estimate for the accuracy of an eigenfunction and an estimate for the approximation error of the lowest eigenvalue can be deduced: There exist $C_1, C_2 > 0$ and $\tilde{\kappa} \in \mathbb{N}$ such that the relation

$$\begin{aligned} E^{(M_S)}_{\min} - E_\kappa &\leq C_1 \langle \Psi^{(M_S)}_{\min} - \Psi_\kappa, H(\Psi^{(M_S)}_{\min} - \Psi_\kappa)\rangle_{\mathcal{L}^2} \\ &\leq C_2 \|\Psi^{(M_S)}_{\min} - \Psi_\kappa\|^2_{\mathcal{H}^1} \end{aligned} \tag{2}$$

holds for all $\kappa \geq \tilde{\kappa}$; see [10–12]. An upper bound for the approximation error in the $\mathcal{H}^1$-norm, i.e. for the right hand side of (2), can then be estimated with the help of the regularity results of [1, 11, 13] similar to (1). This works since the spatial part $\Psi^{(M_S)} := \Psi_{\vec{s}^{(M_S)}}$ of a weak solution of the electronic Schrödinger equation is the Sobolev space $\mathcal{H}^{1/2,1}_{\text{mix}}$ of dominating mixed smoothness and it is even in $\mathcal{H}^{1,1}_{\text{mix}}$ for an electronic wave function of totally parallel spin; see [1] for details.

Such types of spaces are defined for $-\infty < t, r < \infty$, $N \in \mathbb{N}$ by[1]

$$\begin{aligned} \mathcal{H}^{t,r}_{\text{mix}}((\mathbb{R}^3)^N) := \Big\{ f \in \mathcal{S}'((\mathbb{R}^3)^N) \, : \\ \|f\|_{\mathcal{H}^{t,r}_{\text{mix}}} := \int_{(\mathbb{R}^3)^N} |\omega^t_{\text{mix}}(\vec{\mathbf{k}}) \omega^r_{\text{iso}}(\vec{\mathbf{k}}) \hat{f}(\vec{\mathbf{k}})|^2 \, d\vec{\mathbf{k}} < \infty \Big\} \end{aligned}$$

with $\omega_{\text{iso}}(\vec{\mathbf{k}}) := \sqrt{1 + \sum_{p=1}^N |\mathbf{k}_p|^2_\infty}$ and $\omega_{\text{mix}}(\vec{\mathbf{k}}) := \sqrt{\prod_{p=1}^N (1 + |\mathbf{k}_p|^2_\infty)}$. Here, $\mathcal{S}'$ denotes the space of all tempered distributions and $\hat{f}$ denotes the Fourier transform of f. Note that the regularity of a function is directly related to the decay properties of its Fourier transform. In particular, the standard isotropic Sobolev spaces as well as the standard Sobolev spaces of dominating mixed smoothness [14], both generalized to the N-particle case [3, 4], are included in the definition of $\mathcal{H}^{t,r}_{\text{mix}}$. They can be written as

$$\mathcal{H}^r((\mathbb{R}^3)^N) = \mathcal{H}^{0,r}_{\text{mix}}((\mathbb{R}^3)^N) \quad \text{and} \quad \mathcal{H}^t_{\text{mix}}((\mathbb{R}^3)^N) = \mathcal{H}^{t,0}_{\text{mix}}((\mathbb{R}^3)^N),$$

respectively.

In the following, we consider $f \in \mathcal{H}^{t,r}_{\text{mix}}$ with certain decay properties for $|\vec{\mathbf{x}}| \to \infty$. Note that the decay of a function f for $|\vec{\mathbf{x}}|_2 \to \infty$ in the

[1] In particular, the Sobolev space $\mathcal{H}^{t,r}_{\text{mix}}((\mathbb{R}^3)^N)$ is a Hilbert space together with the Hermitian inner product $\langle f \, , \, g\rangle_{\mathcal{H}^{t,r}_{\text{mix}}} := \langle \omega^t_{\text{mix}} \omega^r_{\text{iso}} \hat{f} \, , \, \omega^t_{\text{mix}} \omega^r_{\text{iso}} \hat{g}\rangle_{\mathcal{L}^2}$.

spatial space is directly related to the regularity of the Fourier transform $\hat{f}$ in Fourier space. In this way, for $t + r \geq 0$, $t \geq 0$, $\hat{t} + \hat{r} \geq 0$, $\hat{t} \geq 0$, we define

$$\mathcal{H}^{t,r;\hat{t},\hat{r}}_{\text{mix}} := \left\{ f \in \mathcal{L}^2((\mathbb{R}^3)^N) \,:\, \|f\|_{\mathcal{H}^{t,r;\hat{t},\hat{r}}_{\text{mix}}} := \|f\|_{\mathcal{H}^{t,r}_{\text{mix}}} + \|\hat{f}\|_{\mathcal{H}^{\hat{t},\hat{r}}_{\text{mix}}} < \infty \right\}.$$

In [15] we study its discretization by general sparse grid spaces and the resulting linear approximation properties. To this end, let $\{\phi_{l,\mathbf{j}}\}_{(l,\mathbf{j})\in\mathbb{N}\times\mathbb{Z}^3}$ be a set of multiscale basis functions which span the one-particle space $\mathcal{L}^2(\mathbb{R}^3)$, where the indices l and $\mathbf{j}$ are associated with the scale and the location, respectively. Then, the set of multiscale tensor product basis functions

$$\mathcal{B} := \left\{ \phi_{\vec{l},\vec{\mathbf{j}}} := \bigotimes_{p=1}^{N} \phi_{l_p,\mathbf{j}_p} \right\}_{(\vec{l},\vec{\mathbf{j}})\in\mathbb{N}^N\times(\mathbb{Z}^3)^N}$$

spans the N-particle space $\mathcal{L}^2((\mathbb{R}^3)^N)$. A general finite-dimensional sparse grid space is given by

$$V^{SG}_{\Lambda} := \text{span}\left(\mathcal{B}_{\Lambda} := \left\{ \phi_{\vec{l},\vec{\mathbf{j}}} \in \mathcal{B} \,:\, (\vec{l},\vec{\mathbf{j}}) \in \Lambda \right\} \right) \tag{3}$$

for a finite subset of indices $\Lambda \subset \mathbb{N}^N \times (\mathbb{Z}^3)^N$. The specific choice of the basis functions $\{\phi_{l,\mathbf{j}}\}$ and of the set Λ leads to different variants of sparse grids, e.g. regular sparse grids, energy-norm based sparse grids and dimension adaptive sparse grids [16].

For example, in [15] we construct sparse grid basis sets by a Littlewood-Paley like multiscale decomposition of general hyperbolic cross spaces. In certain cases this leads to Meyer wavelets [17]. For the details of this construction of general sparse grid basis functions we refer to [15, 18].

Now let us go back to the Schrödinger equation ($\mathcal{H}^{1/2,1}_{\text{mix}}$-regularity) and let us additionally assume that the Fourier transform $\hat{\Psi}^{(M_S)}$ is in $\mathcal{H}^{\hat{t},0}_{\text{mix}}$, $\hat{t} > 0$. Let further V^{SG}_{Λ} be an appropriate general sparse grid space with $M = |\Lambda|$ degrees of freedom.[2] Then, the estimate

$$\inf_{\tilde{\Psi}\in V^{SG}_{\Lambda}} \|\Psi^{(M_S)} - \tilde{\Psi}\|_{\mathcal{H}^1} \lesssim \left(\frac{M}{\log_2(M)^{2(N-1)}} \right)^{-\frac{1}{6(1+\tau)}} \|\Psi^{(M_S)}\|_{\mathcal{H}^{\frac{1}{2},1;\hat{t},0}_{\text{mix}}} \tag{4}$$

holds, where $\tau = 3/(2\hat{t})$. For a proof see [15]. We have $\tau \to 0$ if the Fourier transform $\hat{\Psi}^{(M_S)}$ is smooth, i.e. if $\Psi^{(M_S)}$ decays sufficiently fast.[3]

[2] Here, V^{SG}_{Λ} corresponds to the space $V^{0;0}_{L;\tau L}$, $\tau = \frac{3}{2\hat{t}}$, introduced in [15]. There $V^{0;0}_{L;J}$ is spanned by $\{\phi_{\vec{l},\vec{\mathbf{j}}} \,:\, \vec{l} \in \mathcal{I}_L, \vec{\mathbf{j}} \in \mathcal{J}_J(\vec{l})\}$, where $\mathcal{I}_L := \left\{ \vec{l} \in \mathbb{N}^N \,:\, |\vec{l}|_1 \leq L + N - 1 \right\}$, $\mathcal{J}_J(\vec{l}) := \bigcup_{\vec{\imath}\in\mathcal{I}_J} \mathcal{Q}_{\vec{\imath}+\vec{l}+\vec{1}}$, $\mathcal{Q}_{\vec{\alpha}} := \mathcal{Q}_{\alpha_1} \times \cdots \times \mathcal{Q}_{\alpha_N}$ and $\mathcal{Q}_{\alpha} := \{\mathbf{k} \in \mathbb{Z}^3 \,:\, |\mathbf{k}|_{\infty} \leq 2^{\alpha}\}$. In particular with respect to the level parameter L it holds for the number of degrees of freedom $M = |V^{0;0}_{L;\tau L}| = \mathcal{O}(2^{3L(1+\tau)}(\tau L^2)^{N-1})$.

[3] It can be shown that eigenfunctions associated with eigenvalues in the discrete spectrum (bound-states) decay exponentially; compare [11, 19].

Moreover, up to logarithmic terms, the convergence rate is independent of the number of electrons N and is almost the same as in the two-electron case. Thus, we obtain a rate of order $-\frac{1}{6(1+\tau)}$ and hence, due to (2), a rate of order $-\frac{2}{6(1+\tau)}$ for the minimal eigenvalue. Note however that the term $\|\Psi^{(M_S)}\|_{\mathcal{H}^{\frac{1}{2},1;\hat{t},0}_{\mathrm{mix}}}$ and the constants involved in the approximation and complexity order estimates usually depend on the number of particles.

Due to Pauli's principle it is sufficient to consider the partially antisymmetric subspace $\mathfrak{A}^{(M_S)}(V_\Lambda^{SG}) \subset V_\Lambda^{SG}$. This subspace can be spanned by basis functions in the form of the product of two Slater determinants, i.e.

$$\mathfrak{A}^{(M_S)} \bigotimes_{p=1}^{N} \phi_{l_p,\mathbf{j}_p} = \frac{1}{N_\uparrow!} \bigwedge_{p_\uparrow=1}^{N_\uparrow} \phi_{l_{p_\uparrow},\mathbf{j}_{p_\uparrow}} \otimes \frac{1}{N_\downarrow!} \bigwedge_{p_\downarrow=N_\uparrow+1}^{N} \phi_{l_{p_\downarrow},\mathbf{j}_{p_\downarrow}}.$$

In particular, the order for the number of degrees of freedom related to $\mathfrak{A}^{(M_S)}(V_\Lambda^{SG})$ stays the same as in the case of V_Λ^{SG}. However, the involved constant is now reduced by the factor $1/(N_\uparrow!N_\downarrow!)$, i.e. $|\mathfrak{A}^{(M_S)}(V_\Lambda^{SG})| \leq \frac{1}{N_\uparrow!N_\downarrow!}|V_\Lambda^{SG}|$. Furthermore, the order of the achieved accuracy does not change when we switch to the partially antisymmetric case. For details see [3, 4, 15].

3 Adaptive approximation spaces of finite order

General sparse grid spaces can also be employed for many-particle spaces with so-called finite-order weights [7, 9]. The resulting dimension-wise decompositions and discretization schemes then allow to get rid of the remaining exponential dependence on the number of particles with respect to the logarithmic terms in (4), since for finite-order weights of order q the problem of the approximation of an N-particle function reduces to the problem of the approximation of q-particle functions. Note that our construction scheme includes the common CI spaces as a special case, but allows for a more flexible choice of finite-dimensional approximation spaces.

3.1 Particle-wise decomposition

In the following we focus on a particle-wise decomposition of the partially antisymmetric many-particle space $\mathcal{L}^2_{(M_S)}$. Here, for a shorter notation we set $\mathcal{N} := \{1,\dots,N\}$, $\mathcal{N}_\uparrow := \{0,\dots,N_\uparrow\}$ and $\mathcal{N}_\downarrow := \{N_\uparrow+1,\dots,N\}$. Let $\{g_p\}_{p\in\mathcal{N}}$ be $\mathcal{L}^2$-normalized one-particle functions, where $\{g_p\}_{p\in\mathcal{N}_\uparrow}$ as well as $\{g_p\}_{p\in\mathcal{N}_\downarrow}$ are linear independent. Then we have the direct sum decompositions

$$\mathcal{L}^2(\mathbb{R}^3) = U_\uparrow \oplus W_\uparrow \text{ and } \mathcal{L}^2(\mathbb{R}^3) = U_\downarrow \oplus W_\downarrow, \tag{5}$$

where $U_\uparrow := \operatorname{span}(\{g_p\}_{p\in\mathcal{N}_\uparrow})$ and $U_\downarrow := \operatorname{span}(\{g_p\}_{p\in\mathcal{N}_\downarrow})$. With this splitting of the one-particle space, the subspace splitting

$$\mathcal{L}^2_{(M_S)} = \mathfrak{A}^{(M_S)} \left(\bigotimes_{p\in\mathcal{N}_\uparrow} (U_\uparrow \oplus W_\uparrow) \otimes \bigotimes_{p\in\mathcal{N}_\downarrow} (U_\downarrow \oplus W_\downarrow) \right) = \bigoplus_{u\subset\mathcal{N}} \mathcal{W}_u^{(M_S)} \quad (6)$$

follows for the N-particle space, where we set

$$\mathcal{W}_u^{(M_S)} := \mathfrak{A}^{(M_S)} \bigotimes_{p=1}^{N} \mathcal{W}_{u,(p)}^{(M_S)}, \quad \mathcal{W}_{u,(p)}^{(M_S)} := \begin{cases} \operatorname{span}\{g_p\} & \text{for } p \in \mathcal{N} \setminus u, \\ W_\uparrow & \text{for } p \in u \cap \mathcal{N}_\uparrow, \\ W_\downarrow & \text{for } p \in u \cap \mathcal{N}_\downarrow. \end{cases}$$

Correspondingly, any function $f \in \mathcal{L}^2_{(M_S)}$ can be decomposed as

$$f = \sum_{u\subset\mathcal{N}}^{N} \mathfrak{A}^{(M_S)}(F_u) = \sum_{u\subset\mathcal{N}}^{N} \mathfrak{A}^{(M_S)} \left(\vec{\mathbf{y}} \mapsto f_u(\vec{\mathbf{y}}_u) \prod_{p\in\mathcal{N}\setminus u} g_p(\mathbf{y}_p) \right) \quad (7)$$

with the help of appropriate linear projections such that $\mathfrak{A}^{(M_S)} F_u \in \mathcal{W}_u^{(M_S)}$ and $f_u \in \bigotimes_{p\in u} \mathcal{W}_{u,(p)}^{(M_S)}$. Moreover, in the case of orthogonal direct sums $V_\uparrow \oplus W_\uparrow$, $V_\downarrow \oplus W_\downarrow$ and orthonormal $\{g_p\}_{p\in\mathcal{N}_\uparrow}$, $\{g_p\}_{p\in\mathcal{N}_\downarrow}$, the orthogonality relation $\langle F_u \,,\, F_{u'} \rangle = 0$ holds for all $u \neq u'$. Note that a similar type of a particle-wise decomposition was introduced by Sinanoğlu in quantum chemistry for the analysis of many-electron wave functions [20]. There, orthogonal Hartree-Fock orbitals were suggested as one-particle functions $\{g_p\}_{p\in\mathcal{N}}$. Note furthermore the close relation of this particle-wise decomposition to the classical ANOVA decomposition [8].

Now, we consider decompositions

$$\mathcal{L}^2(\mathbb{R}^3) = U_\uparrow + W \text{ and } \mathcal{L}^2(\mathbb{R}^3) = U_\downarrow + W, \quad (8)$$

which involve non-direct sums instead of the direct sums in (5). Then, similar to (6) we obtain

$$\mathcal{L}^2_{(M_S)} = \mathfrak{A}^{(M_S)} \left(\bigotimes_{p\in\mathcal{N}_\uparrow} (U_\uparrow + W) \otimes \bigotimes_{p\in\mathcal{N}_\downarrow} (U_\downarrow + W) \right) = \sum_{u\subset\mathcal{N}} \mathcal{W}_u^{(M_S)} \quad (9)$$

for the N-particle space.[4] Here, in contrast to (6) and (7), a corresponding decomposition of a function in $\mathcal{L}^2_{(M_S)}$ is no longer unique. However, appropriate weighted norms can still be introduced with the help of the infimum over all decompositions of a function; see also [21]. This is discussed in the following.

[4] Note that we have $\mathcal{W}_{u,(p)}^{(M_S)} = \begin{cases} \operatorname{span}\{g_p\} & \text{for } p \in \mathcal{N} \setminus u, \\ W & \text{for } p \in u. \end{cases}$

3.2 Weighted many-particle approximation spaces

In the setting of (8) and (9) for $t+r \geq 0$, $t \geq 0$, $\{g_p\}_{p\in\mathcal{N}}$ and non-negative $\{\gamma_u\}_{u\subset\mathcal{N}}$, weighted partially antisymmetric many-particle spaces can be introduced by

$$\mathcal{H}^{t,r;\hat{t},\hat{r};(M_S)}_{\mathrm{mix},\{g_p\},\{\gamma_u\}}((\mathbb{R}^3)^N) := \left\{ f \in \mathcal{L}^2_{(M_S)} \,:\, \|f\|_{\mathcal{H}^{t,r;\hat{t},\hat{r}}_{\mathrm{mix},\{g_p\},\{\gamma_u\}}} < \infty \right\}$$

with the norm

$$\|f\|^2_{\mathcal{H}^{t,r;\hat{t},\hat{r};(M_S)}_{\mathrm{mix},\{g_p\},\{\gamma_u\}}} := \inf\Bigg\{ \sum_{u\subset\mathcal{N}} \gamma_u^{-1} \|\tilde{f}_u\|^2_{\mathcal{H}^{t,r;\hat{t},\hat{r}}_{\mathrm{mix}}} \,:\, \{\tilde{f}_u \in W^{|u|}\}_{u\subset\mathcal{N}}, f = \sum_{u\subset\mathcal{N}} \mathfrak{A}^{(M_S)}\big(\vec{\mathbf{y}} \mapsto \tilde{f}_u(\vec{\mathbf{y}}_u) \prod_{p\in\mathcal{N}\setminus u} g_p(\mathbf{y}_p)\big)\Bigg\}.$$

Note that $\{\gamma_u\}_{u\subset\mathcal{N}}$ is called a set of weights of finite order q if $\gamma_u = 0$ for all γ_u with $|u| > q$. In that case, the problem of the approximation of an N-particle function reduces to the problem of the approximation of $\binom{N}{q}$ q-particle functions. In the framework of the decomposition (9) we use finite-order weights $\{\gamma_u\}_{u\subset\mathcal{N}}$ to switch certain subspaces $\mathcal{W}_u^{(M_S)}$ on or off, i.e. we set

$$\mathcal{V}^{(M_S)}_{\{\gamma_u\}_u} := \sum_{u\subset\mathcal{N},\gamma_u>0} \mathcal{W}_u^{(M_S)}. \tag{10}$$

Clearly, $\mathcal{V}^{(M_S)}_{\{\gamma_u\}_u} \subset \mathcal{L}^2_{(M_S)}$ since $\{u \subset \mathcal{N} \,:\, \gamma_u > 0\}$ is a subset of $\{u \subset \mathcal{N}\}$. The restriction of the decomposition (9) via the finite-order weights $\{\gamma_u\}_{u\subset\mathcal{N}}$ resembles a first step towards approximation, but the involved subspaces $\mathcal{W}_u^{(M_S)}$ are still infinite-dimensional and need further discretization. Thus, the idea is to construct a finite-dimensional subspace of $\mathcal{V}^{(M_S)}_{\{\gamma_u\}_u}$ by choosing a specific finite-dimensional subspace of $\mathcal{W}_u^{(M_S)}$ for each u with $\gamma_u > 0$ separately. Altogether, this induces a discretization of $\mathcal{V}^{(M_S)}_{\{\gamma_u\}_u}$.

To this end, let $\{\phi_\nu\}_{\nu\in\mathbb{N}}$ be an appropriate frame of $W = \mathcal{L}^2(\mathbb{R}^3)$. Note that for reasons of simplicity we switch here from the notation with two indices $(l,\mathbf{j})$ associated to level and location as in Section 3 to a notation with just one unspecified index ν. Then, for each $u = \{p_1 < \cdots < p_{|u|}\} \subset \mathcal{N}$ with $\gamma_u > 0$ we introduce a finite-dimensional subspace $\mathcal{W}^{(M_S)}_{u,\mathcal{B}_u}$ of $\mathcal{W}_u^{(M_S)}$ by the span of the finite set $\mathcal{B}_u$ of partially antisymmetric N-particle functions. Here, $\mathcal{B}_u$ is chosen as appropriate finite subset of

$$\mathcal{B}_u^{(M_S)} := \left\{ \mathfrak{A}^{(M_S)}\Big(\vec{\mathbf{y}} \mapsto \prod_{q=1}^{|u|} \phi_{\nu_q}(\mathbf{y}_{p_q}) \prod_{p\in\mathcal{N}\setminus u} g_p(\mathbf{y}_p)\Big) \right\}_{(\nu_1,\ldots,\nu_{|u|})\in\mathbb{N}_u^{(M_S)}}, \tag{11}$$

where

$$\mathbb{N}_u^{(M_S)} := \left\{(\nu_1, \ldots, \nu_{|u|}) \in \mathbb{N}^{|u|} \,:\, \nu_1 < \ldots < \nu_{n_\uparrow}, \nu_{n_\uparrow+1} < \cdots < \nu_{|u|}\right\}$$

with $n_\uparrow := |u \cap \mathcal{N}_\uparrow|$. Note that for a shorter notation we indicate subspaces directly by their spanning system instead of a set of indices as in (3). In this way, a finite-dimensional subspace of $\mathcal{V}_{\{\gamma_u\}_u}^{(M_S)}$ can be defined by

$$V_{\{\gamma_u\}_u, \{\mathcal{B}_u\}_u}^{SG} := \sum_{u \subset \mathcal{N}, \gamma_u > 0} \mathcal{W}_{u, \mathcal{B}_u}^{(M_S)}. \tag{12}$$

Note that the specific choice of the one-particle functions $\{g_p\}_{p \in \mathcal{N}}$, the multiscale frame $\{\phi_\nu\}_{\nu \in \mathbb{N}}$, the weights $\{\gamma_u\}_{u \subset \mathcal{N}}$ and the family of finite systems $\{\mathcal{B}_u\}_{u \subset \mathcal{N}, \gamma_u > 0}$ is still open.

For the $\{g_p\}_{p \in \mathcal{N}}$ we employ a set of non-orthogonal Hartree-Fock orbitals, which are given in terms of atomic orbitals. In particular, these orbitals are written in the form of a finite expansion of isotropic and modulated Gaussians; see [15, 22]. The specific choices of $\{\phi_\nu\}_{\nu \in \mathbb{N}}$, $\{\gamma_u\}_{u \subset \mathcal{N}}$ and $\{\mathcal{B}_u\}_{u \subset \mathcal{N}, \gamma_u > 0}$ are discussed in the following.

3.3 Multiscale Gaussian frame

For the one-particle frame $\{\phi_\nu\}_{\nu \in \mathbb{N}}$ we employ a wavelet-like frame based on Gaussians, which exhibits exponential decay in real space as well as in Fourier space and in particular allows for local adaptivity and the computation of all inner products by analytic formulae.[5] We introduce this wavelet-like frame in the following.

By dilation and translation, we define the functions

$$\varphi_{\sigma,c,l,\mathbf{j}}(\mathbf{x}) := \left(c2^l\right)^{\frac{3}{2}} \varphi_\sigma(c2^l\mathbf{x} - \mathbf{j})$$

for $c > 0$, $l \in \mathbb{N}_0$ and $\mathbf{j} \in \mathbb{Z}^3$, where we employ for the generating function $\varphi_\sigma(\mathbf{x}) := (\sigma\sqrt{\pi})^{-\frac{3}{2}} e^{-\frac{1}{2\sigma^2}|\mathbf{x}|_2^2}$ a normalized isotropic Gaussian. Moreover, we introduce a wavelet-like function in terms of generating functions of two scales by

$$\psi_\sigma(\mathbf{x}) := C_{\psi_\sigma}\left(\varphi_{\frac{\sigma}{2}}(\mathbf{x}) - 2^{-\frac{3}{2}}\varphi_\sigma(\mathbf{x})\right),$$

with the normalization constant $C_{\psi_\sigma} = (1 - \frac{16}{25}\gamma\sqrt{5} + \gamma^2)^{-\frac{1}{2}}$. In particular, we define the functions

$$\psi_{\sigma,c,l,\mathbf{j}}^{[\mathbf{z}]}(\mathbf{x}) := \left(c2^l\right)^{\frac{3}{2}} \psi_\sigma(c2^l\mathbf{x} - \mathbf{j} - \tfrac{1}{2}\mathbf{z})$$

by dilation and translation for $c > 0$, $l \in \mathbb{N}_0$, $\mathbf{j} \in \mathbb{Z}^3$ and $\mathbf{z} \in \mathcal{Z} := \{0,1\}^3 \backslash \mathbf{0}$. Note that $\psi_{\sigma,c,l,\mathbf{j}}^{[\mathbf{z}]}$ is normalized and its zeroth and first moments

[5] Note that from the Balian-Low theorem there follows that no orthonormal frame with exponential decay in both real space and in Fourier space exists.

vanish. Finally, we introduce a wavelet-like frame by

$$\mathfrak{b}_{\sigma,c} := \left\{\varphi_{\sigma,c,0,\mathbf{j}} : \mathbf{j} \in \mathbb{Z}^3\right\} \cup \bigcup_{\mathbf{z}\in\mathcal{Z}} \left\{\psi^{[\mathbf{z}]}_{\sigma,c,l,\mathbf{j}} : l \in \mathbb{N}_0, \mathbf{j} \in \mathbb{Z}^3\right\}. \tag{13}$$

Here, the scaling-like functions $\varphi_{\sigma,c,0,\mathbf{j}}$ are enumerated by $\mathbf{j}$ where the wavelet-like functions $\psi^{[\mathbf{z}]}_{\sigma,c,l,\mathbf{j}}$ are enumerated by $(l,\mathbf{j},\mathbf{z})$ due to its construction. Now, to invoke (11) we need an enumeration of the overall set $\mathfrak{b}_{\sigma,c}$. We assume ν to be the enumeration index, i.e. $\{\phi_\nu\}_{\nu\in\mathbb{N}} = \mathfrak{b}_{\sigma,c}$.

Note further that a frame like $\mathfrak{b}_{\sigma,c}$ can particularly be seen as an *approximation* to a Meyer wavelet basis [23]. In [4] we studied the application of an orthonormal tensor product basis built from Meyer wavelets and Meyer scaling functions in practice. It turned out that, although the wavelet system allows us to resolve the cusps locally, the sub-exponential decay of the basis functions in real space and the expensive numerical integration of the one-particle operator integrals and in particular of the two-particle operator integrals leads to impractically huge constants. Now with the frame $\mathfrak{b}_{\sigma,c}$ we are able to substantially reduce the involved constants as we will see later.

3.4 Adaptive scheme

We choose the weights $\{\gamma_u\}_{u\subset\mathcal{N}}$ in an a priori way based on quantum chemistry knowledge. To be precise, we employ a specific set of finite-order weights of order three so that we obtain a sum of subspaces in the form

$$\mathcal{V}^{(M_S)}_{three} := \mathcal{V}^{zero}+\mathcal{V}^{one}+\mathcal{V}^{two\uparrow\downarrow}+\mathcal{V}^{two\uparrow\uparrow}+\mathcal{V}^{three} \subset \sum_{u\subset\mathcal{N},|u|\leq 3} \mathcal{W}^{(M_S)}_u, \tag{14}$$

where

$$\mathcal{V}^{zero} := \mathcal{W}^{(M_S)}_{\emptyset},\ \mathcal{V}^{one} := \sum_{p_1\in\mathcal{N}} \mathcal{W}^{(M_S)}_{\{p_1\}},\ \mathcal{V}^{two\uparrow\downarrow} := \sum_{p_1\in\mathcal{N}_\uparrow} \sum_{p_2\in\mathcal{N}_\downarrow} \mathcal{W}^{(M_S)}_{\{p_1,p_2\}},$$

$$\mathcal{V}^{two\uparrow\uparrow} := \sum_{p_1,p_2\in\mathcal{N}_\uparrow} \mathcal{W}^{(M_S)}_{\{p_1,p_2\}} + \sum_{p_1,p_2\in\mathcal{N}_\downarrow} \mathcal{W}^{(M_S)}_{\{p_1,p_2\}},$$

$$\mathcal{V}^{three} := \sum_{p_1,p_2\in\mathcal{N}_\uparrow} \sum_{p_3\in\mathcal{N}_\downarrow} \mathcal{W}^{(M_S)}_{\{p_1,p_2,p_3\}} + \sum_{p_1\in\mathcal{N}_\uparrow} \sum_{p_2,p_3\in\mathcal{N}_\downarrow} \mathcal{W}^{(M_S)}_{\{p_1,p_2,p_3\}},$$

compare (10).

The sets $\{\mathcal{B}_u\}_{u\subset\mathcal{N},\gamma_u>0}$ are then constructed by an heuristic h-adaptive scheme in an a posteriori fashion. We denote the resulting sequence of finite-dimensional spaces by

$$\left\{V^{SG}_\kappa := V^{SG}_{\{\gamma_u\}_u,\{\mathcal{B}^{[\kappa]}_u\}_u} \subset \mathcal{V}^{(M_S)}_{\{\gamma_u\}_u}\right\}_{\kappa\in\mathbb{N}_0}.$$

To this end, we first choose the initial spanning system $\{\mathcal{B}^{[0]}_u\}_{u,\gamma_u>0}$. The

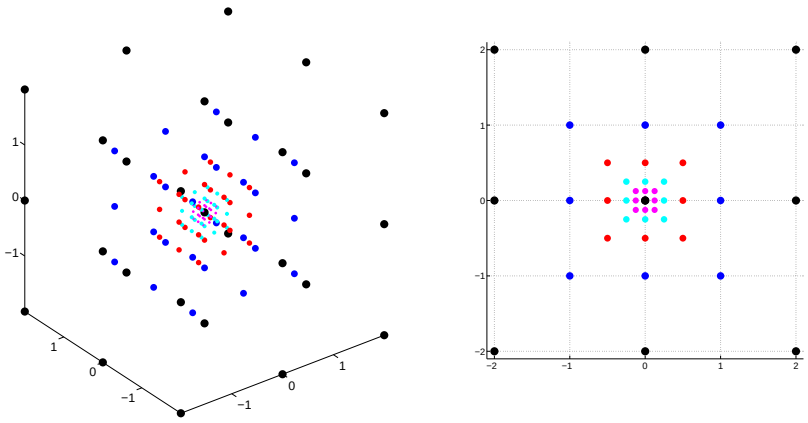

Figure 1: Localization peaks of basis functions in $\mathfrak{b}^{(5)}_{1,1/2}$. On the right hand side we depict a slice plane, i.e. the (x_1, x_2)-plane, of the view on the left hand side.

initial approximation space V_0^{SG} is built with the help of one-particle subspaces (with just a few degrees of freedom) which provide an accurate representation of atomic orbitals. We define those one-particle subspaces by the span of the initial system

$$\mathfrak{b}^{(L)}_{\sigma,c} := \{\varphi_{\sigma,c,0,\mathbf{j}} \,:\, |\mathbf{j}|_\infty \leq 1\} \cup \bigcup_{\mathbf{z}\in\mathcal{Z}} \left\{\psi^{[\mathbf{z}]}_{\sigma,c,l,\mathbf{j}} \,:\, l \leq L-2, \mathbf{j} = -\mathbf{z}\right\} \subset \mathfrak{b}_{\sigma,c}, \tag{15}$$

see Figure 1. Now, let us consider an atomic system with N electrons and a nucleus of atomic charge Z_1 centered at $\mathbf{R}_1$, where we assume $\mathbf{R}_1 = \mathbf{0}$ for reasons of simplicity. Let the parameters σ, c and L be fixed. Then, in the case of spanning systems associated with finite-order weights $\gamma_u > 0$ with $|u| = 1$ (i.e. related to $\mathcal{V}^{one}$), we set

$$\mathcal{B}^{[0]}_{\{p_1\}} = \mathcal{B}^{(M_S)}_{\{p_1\}} \cap \left\{\mathfrak{A}^{(N,M_S)}\Big(\vec{\mathbf{y}} \mapsto w(\mathbf{y}_{p_1}) \prod_{q\in\mathcal{N}\setminus\{p_1\}} v_q(\mathbf{y}_q)\Big) \,:\, \phi \in \mathfrak{b}^{(L)}_{\sigma,c}\right\}$$

for $p_1 \in \mathcal{N}$. For spanning systems according to finite-order weights $\gamma_u > 0$, $|u| \geq 2$ the idea is to employ certain tensor product functions with localization peaks at or close to the electronic cups. In this way, for example for the case of $\mathcal{V}^{two\uparrow\downarrow}$, we set

$$\mathcal{B}^{[0]}_{\{p_1,p_2\}} = \mathcal{B}^{(M_S)}_{\{p_1,p_2\}} \cap \left\{\mathfrak{A}^{(N,M_S)}\Big(\vec{\mathbf{y}} \mapsto \phi(\mathbf{y}_{p_1})\phi(\mathbf{y}_{p_2}) \prod_{q\in\mathcal{N}\setminus\{p_1,p_2\}} \phi_q(\mathbf{y}_q)\Big) \,:\, \phi \in \mathfrak{b}^{(L)}_{\sigma,c}\right\},$$

for $p_1 \in \mathcal{N}_\uparrow$, $p_2 \in \mathcal{N}_\downarrow$; see also Figure 2 (left). The sets $\mathcal{B}_{\{p_1,p_2\}}$ and $\mathcal{B}_{\{p_1,p_2,p_3\}}$ related to $\mathcal{V}^{two\uparrow\uparrow}$ and $\mathcal{V}^{three}$, as well as the initial sets in the case of two atoms, are constructed in a similar way. Next, we invoke a coarsening step on the a priori chosen set $\{\mathcal{B}_u^{[0]}\}_{u,\gamma_u>0}$. Finally, the sequence of spanning systems $\{\mathcal{B}_u^{[\kappa]} \subset \mathcal{B}_u^{(M_S)}\}_{\kappa\in\mathbb{N}}$ is build by a simple h-adaptive refinement scheme in an a posteriori fashion. To this end, the solution of the general linear eigenvalue problem and a refinement and expansion of the spanning system is performed iteratively; for details see [15]. The resulting sequence of approximation spaces

$$\left\{V_\kappa^{SG} = V^{SG}_{\{\gamma_u^{[\kappa]}\}_u,\{\mathcal{B}_u^{[\kappa]}\}_u}\right\}_{\kappa>0}$$

hopefully gives an efficient representation of the involved cusps. Figure 2 (right) shows the localization peaks of the basis set $\mathcal{B}^{[9]}_{\{1,2\}}$ constructed by our algorithm in the case of the He atom. Note that the span of $\mathcal{B}^{[9]}_{\{1,2\}}$ is a subspace of $\mathcal{V}^{two\uparrow\downarrow}$.

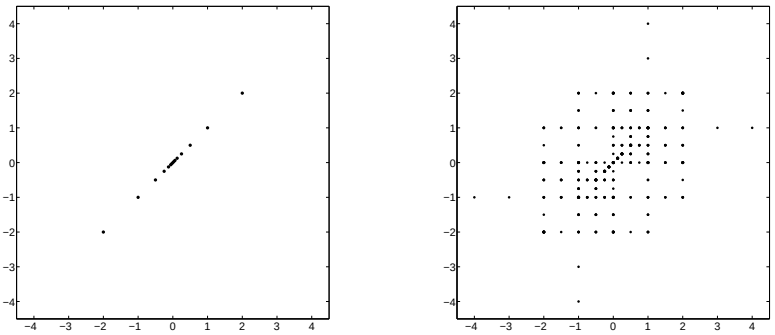

Figure 2: Localization peaks of frame functions in the case of He, where we depict the $(x_{1,(1)}, x_{2,(1)})$-plane. Left: Initial set $\mathcal{B}^{[0]}_{\{1,2\}}$ for $L = 7$ and $c = \frac{1}{2}$. Right: Basis set $\mathcal{B}^{[9]}_{\{1,2\}}$ constructed by our adaptive algorithm.

For technical details of our adaptive scheme to build the sequence of approximation spaces $\{V_\kappa^{SG}\}$ see [15]. For a further reading on adaptive wavelet techniques see [24].

4 Numerical methods and experiments

For each finite-dimensional subspace V_κ^{SG} the Galerkin discretization results in a generalized linear eigenvalue problem, i.e. $Av = EBv$. We compute the entries of the corresponding stiffness A and the mass matrices

B with the help of the so-called Löwdin rules [25] for Slater determinants. Here, an N-particle integral over a product of Slater determinants is reduced to the computation of determinants of matrices with entries put together from values of certain one- and two-particle integrals. Furthermore, we perform the assembly of the system matrices A and B in parallel in a straightforward way. For the parallel solution of the eigenvalue problem $Av = EBv$ we invoke the *scalable library for eigenvalue problem computations* (SLEPc) [26]. This software package provides a wrapper to the software library BLOPEX, which is an implementation of the parallelized *locally optimal block preconditioned conjugate gradient* method (LOBPCG) [27]. For the molecules considered in this article, we have to treat full matrices. Thus, we invoke a Cholesky decomposition as implemented in the software package PLAPACK [28] to perform preconditioning in an efficient way.

4.1 Applications

In the following we apply our novel method to several atomic and diatomic systems with up to six electrons. Here, we aim at the determination of the total energies of the considered molecular systems up to the so-called chemical accuracy, i.e. $1\,\mathrm{kcal/mol} \approx 1.595_{-3}\,\mathrm{hartree}$. Note that the main task is to efficiently describe electron correlation [29]. We give the results of our numerical approach in Table 1 and Figure 3. They suggest that our new method is indeed convergent and that the measured rates are in the expected range. In particular, the results demonstrate that our new method allows to efficiently describe electron-nuclei and electron-electron cusps. Nevertheless, we see a dependence of the involved constants on the molecular system size.

For the two- and three-electron systems chemical accuracy is easily reached. For four-electron systems we obtain an approximation error of a size smaller than ten milli-hartree. In particular, we obtain in the case of two-electron, three-electron and four-electron systems proportions E_c of the correlation energy larger than 98 %, 96 % and 88 %, respectively. In the case of the five- and six-electron molecular systems, our results seem to be still in the pre-asymptotic range. Note here that the involved number of degrees of freedom is restricted by physical memory limitations. Nevertheless, for the five- and six-electron systems proportions E_c of the correlation energies are achieved in the range of 71 % to 87 %.

Note furthermore that for the studied systems Li, Be, LiH, B, BeH and BH the size of the approximation error of our new method is less than the error obtained by VMC methods which employ a single-determinant Jastrow-Slater trial wave function. The better accuracy could be expected since the present approach improves the reference single-determinant in an exact way like CI and CC methods, instead of employing an inexact multiplicative Jastrow factor ansatz. Moreover, our results are in the range of those computed by diffusion Monte Carlo (DMC) methods which are

Table 1: Numerical results for the total energy $\tilde{E}_{tot}$ and the Hartree-Fock energy $\tilde{E}_{tot}^{HF}$. With respect to the applied parameters see Table 2. The *exact* values for the total energies E_{tot} and the Hartree-Fock limits E_{tot}^{HF} are taken from literature; see [15] and the references therein. We give the proportion of correlation energy $E_c := \frac{\tilde{E}_{tot} - E_{tot}^{HF}}{E_{tot} - E_{tot}^{HF}}$ in percentage. E_{tot}^{VMC} are the results computed by variational quantum Monte Carlo methods which are based on a single-determinant Jastrow-Slater trial wave function. These are taken from [30–32].

	$\tilde{E}_{tot}$	E_{tot}	$\tilde{E}_{tot}^{HF}$	E_{tot}^{HF}	E_c	E_{tot}^{VMC}
He	-2.90330	-2.90372	-2.86166	-2.86168	99.00	
H_2	-1.17376	-1.17447	-1.12854	-1.13366	98.26	
(^3S)He	-2.17522	-2.17523	-2.17424	-2.17420	99.10	
$(b^3\Sigma_u^+)H_2$	-0.89704	-0.89708	-0.89057	-0.89288	99.14	
He_2^+	-4.99305	-4.99464	-4.91647	-4.92285	97.78	
$(^4P^0)$Li	-5.36764	-5.36801	-5.35830	-5.35830	96.18	
Li	-7.47702	-7.47806	-7.43271	-7.43273	97.58	-7.47683
Be	-14.65978	-14.66736	-14.57296	-14.57302	90.94	-14.63110
LiH	-8.06084	-8.07055	-7.97054	-7.98735	88.05	-8.04593
B	-24.63768	-24.65391	-24.52921	-24.52906	87.00	-24.60562
BeH	-15.22016	-15.24680	-15.04328	-15.15318	71.55	-15.21210
C	-37.80020	-37.84500	-37.65886	-37.68862	71.35	-37.81471
BH	-25.26089	-25.28790	-25.08382	-25.13195	82.68	-25.21220
Li_2	-14.96810	-14.99540	-14.86166	-14.87152	77.97	-14.98255

Table 2: Parameters for the frame $\mathfrak{b}_{\sigma,c}$ and its subset $\mathfrak{b}_{\sigma,c}^{(L)}$; compare (13) and (15). For all systems we set $\sigma = 1$. For all diatomic systems we set $c = \frac{2}{R}$. The respective bond distances R are given in bohr.

	He	(^3S)He	$(^4P^0)$Li	Li	Be	B	C
c	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	1	$\frac{1}{4}$	1	1
L	7	7	7	6	8	7	7

	H_2	$(b^3\Sigma_u^+)H_2$	He_2^+	LiH	BeH	BH	Li_2
R	1.4	2.0	2.042	3.015	2.537	2.329	5.051
L	5	5	6	6	7	7	7

based on a single-determinant Jastrow-Slater trial wave function; compare [30–32].

5 Concluding remarks

In this article we introduced and studied new tensor product multiscale many-particle spaces with finite-order weights and applied them in the numerical treatment of the electronic Schrödinger equation. These spaces are constructed from a particle-wise subspace splitting of the N-particle space. In particular, this construction provides a systematic improvement of a nonlinear rank-1 approximation by its combination with a tensor product multiscale approximation scheme and allows for convergence

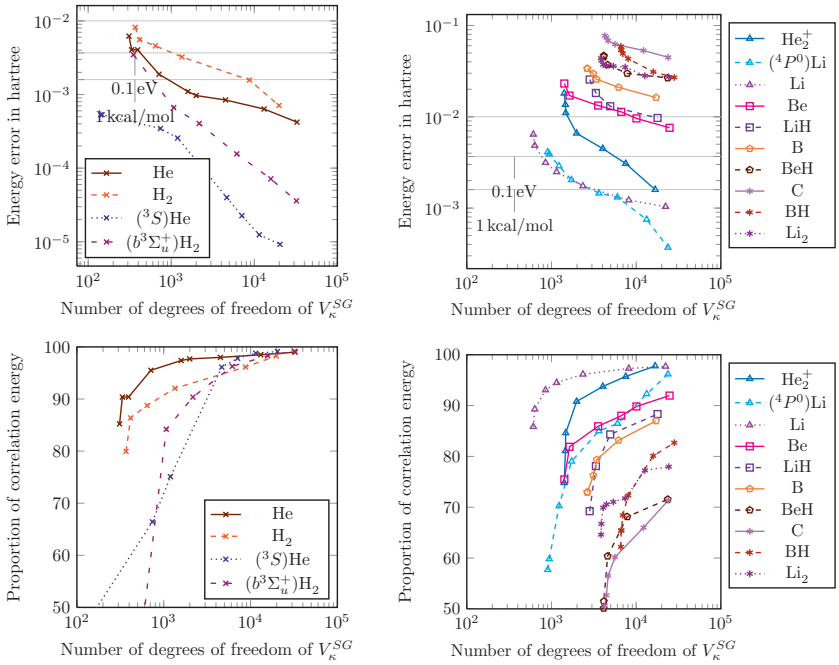

Figure 3: Error of the approximately computed energy of the ground-state of several atomic and diatomic systems with up to six electrons.

with guaranteed approximation rates. We demonstrated these rates numerically for atoms and diatomic molecules with up to six electrons. Note that to our knowledge this is the first time that systems with more than two electrons were successfully treated by direct numerical approximation by means of an application of tensor product multiscale bases in the framework of ab initio methods (except for HF and DFT methods).

Both the multiscale frame and the adaptive scheme can probably still be improved. Multi-wavelet like frames based on Hermite-Gaussian functions together with an h- and p-adaptive refinement strategy may lead to improved approximation properties. Furthermore, from a theoretical point of view, such an adaptive best M-term approximation requires a new, not yet existing mixed Besov regularity theory for the electronic Schrödinger equation. Here, exponential Jastrow factors in the two-electron case have been studied in [33] to deduce some preliminary assertions on possible convergence rates. Their results yield a convergence rate of order $-1/2$ for the related two-particle correlation functions, compared to a rate of order $-1/4$ when applying a linear approximation scheme. Moreover, our scheme might be extended to varying weights and thereby subspaces in an adaptive way (particle-wise adaptivity) similar

to dimension-wise adaptive approaches for high-dimensional quadrature [34, 35]. Also, an adaptive scheme which applies multiscale frames including ridgelet-like two-particle functions [36], the application of two-particle functions for the electron-electron cusps similar to the R12/F12 methods [37] and the extended geminal model [38] could be promising for the future.

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