

Wavelets for density matrix computation in electronic structure calculation [☆]

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Abstract

This paper is concerned with demanding calculations of electronic structures. We give a brief introduction to the basics of electronic structure calculation based on the electronic multi-particle Schrödinger equation. We describe the structures of Hartree–Fock, Kohn–Sham and hybrid models for closed shell systems, the aufbau principle and the self consistent field iteration. While traditional methods for computing the orbitals are scaling cubically w.r.t. the number of electrons, the computation of the density matrix offers the opportunity to achieve linear complexity. We describe several iteration schemes for the computation of the density matrix. We briefly present the concept of best n -term approximation and summarize recent regularity results obtained by the authors. They show that the density matrix is in mixed Besov spaces $B_{\tau,\tau}^s$. Adaptive sparse grid approximation will reduce the complexity by several magnitudes. We propose fast methods for matrix computations as e.g. wavelet matrix compression. Finally, first numerical experiments demonstrate the behavior of the described iteration schemes for computing the density matrix.

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1. Introduction

Modern developments in technology and sciences are demanding for numerical simulation of molecular structures. Among the most prominent and modern developments there are molecular biology, nano-science and design of semiconductor devices. Even for macroscopic models in continuum mechanics unknown parameters are determined by numerical simulation on a microscopic scale. A multi-scale modeling comes up with a hierarchy of models, where the parameters for the macroscopic models are calibrated by a computation on a microscopic scale. On a molecular or atomic scale, physical phenomena are governed by the laws of quantum mechanics. Therefore any determination of molecular parameters should be based on a reliable computational tool simulating the quantum mechanical phenomena accurately. This is the ambitious principle of *ab initio methods*. The model equations should be based only on the

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very few fundamental laws of quantum mechanics, essentially the many particle *Schrödinger equation*, which is by now the only commonly accepted fundamental basis.

In contrast to the increasing interest in modern technologies, ab initio computation is not a new subject. In fact it has an impressive 70 years old history. Based on the fundamental work of Dirac, Hartree and Slater, who established the *stationary electronic Schrödinger equation* and the approximation of the wave function by Slater determinants, computational effort has started immediately with the advent of electronic computers for solving problems in chemistry. The surprising success of recent ab initio computations is the result of systematic developments in quantum chemistry using Gaussian type basis functions and additionally the development of density functional theory by Kohn and co-authors, which simplifies the equations drastically. The work of Pople and Kohn was awarded in 1998 by the noble prize in chemistry, not forgetting an armada of scientists who substantially contributed to the development. Surprisingly, this challenging field is not well known in the numerical analysis community yet, neither has attracted many mathematicians working in this field.

Gaussian type basis functions are commonly used in computational quantum chemistry. Already relatively few of these basis functions provide highly accurate results. They have been optimized up to an efficiency which is far better than that one of systematic basis functions based on Cartesian coordinates. Only for periodic problems, e.g. band structure calculations for crystals, plane wave basis sets are most prominent, in conjunction with pseudo-potentials. All these methods are scaling at least cubically w.r.t. the number of electrons N . This scaling is a bottleneck for computing large systems including several thousands of electrons. Recently, ideas have been proposed claiming linear scaling. These methods are working quite well for insulating systems and small sets of highly localized Gaussian basis functions [1,27,43]. Moreover, recent advances in post Hartree–Fock computation have reduced an $\mathcal{O}(N^7)$ to linear complexity [50,51]. Nevertheless, including more and more diffusive Gaussian basis functions would ruin the efficiency of linear scaling methods completely. For the computation of extremely large systems within the framework of density functional theory, wavelet basis functions might offer a perspective [11]. We will show how these methods are scaling linearly, in a crude sense, not only with the number of particles but also w.r.t. the number of basis functions. Therefore the present approach might be quite robust. It might work also in cases where linear scaling methods with Gaussian basis functions fail. To achieve this scaling we exploit two properties of multi-scale bases. Firstly, a sparse grid approximation is relieving the curse of dimensions. This includes also the fast evaluation and compression of nonlocal operators. Secondly, the concept of best \mathcal{N} -term approximation is optimizing the number of basis functions. Theoretical results for electronic structure calculations obtained by the authors are mentioned. These results (Theorems 11, 12) indicate the potential of an adaptive tensor-product wavelet scheme (sparse grid approximation) for linear scaling computations. The sparse grid approximation reduces the complexity of computations in \mathbb{R}^6 and \mathbb{R}^3 . Since wavelet bases are multi-scale bases they can even separate between an inner-atomic scale and a larger molecular scale; a feature which should be more exploited [7]. In future, research should look for possibilities to supplement traditional Gaussian basis implementations by the new ideas [21,49].

The present article aims to give a very brief introduction into electronic structure calculation and linear scaling methods. We discuss linear scaling wavelet methods, summarizing recent approximation results in [21]. For the sake of brevity, we drop several topics which are very important, as pseudo-potentials, periodic structures, post Hartree–Fock methods, Kronecker product approximation and many more. The reader should be aware that we have simplified the problem at many instances, and a powerful implementation will be an extremely complex task.

2. Electronic structure calculation

The properties of a physical system of N electrons with spin s_i , $i = 1, \dots, N$, are completely described by a *state- or wave-function*

$$(\mathbf{x}_1, s_1; \dots; \mathbf{x}_N, s_N) \mapsto \Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_N, s_N) \in \mathbb{C}.$$

Each particle i is described by its spatial coordinates $\mathbf{x}_i = (x_{i,1}, x_{i,2}, x_{i,3}) \in \mathbb{R}^3$ and a spin variable $s_i = \pm \frac{1}{2}$. The motion of the N electrons is influenced by an exterior electric field caused by M positively charged nuclei. According to the *Born–Oppenheimer approximation* we treat them as classical particles with charges Z_j at fixed positions $\mathbf{R}_j \in \mathbb{R}^3$, $j = 1, \dots, M$.

Let $H^1((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N)$ denote the Sobolev space of order 1 and $\bigwedge_{i=1}^N L_2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$ the subspace of antisymmetric functions in $L_2((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N)$. Under the above assumptions Ψ satisfies the *electronic Schrödinger equation*. Introducing *atomic units* it has the form

$$\mathcal{H}\Psi := \sum_{i=1}^N \left[-\frac{1}{2}\Delta_i - \sum_{j=1}^M \frac{Z_j}{|\mathbf{x}_i - \mathbf{R}_j|} + \sum_{j<i}^N \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \right] \Psi = E\Psi, \tag{1}$$

where the state function

$$\Psi \in H_a^1 = H^1\left(\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right)^N\right) \cap \bigwedge_{i=1}^N L_2\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right) \tag{2}$$

satisfies $\langle \Psi, \Psi \rangle = 1$.

The electronic Schrödinger equation is an eigenvalue problem for a linear partial differential operator. The fact that there is a discrete spectrum explains all quantum effects observed in several experiments as e.g. spectral lines. The *ground state energy* E_0 is given by

$$E_0 = \min\{\langle \mathcal{H}\Psi, \Psi \rangle : \Psi \in H_a^1, \langle \Psi, \Psi \rangle = 1\},$$

and the Schrödinger equation for the corresponding eigenfunction Ψ can be cast into a variational problem

$$\Psi = \arg \min\{\langle \mathcal{H}\Psi, \Psi \rangle : \Psi \in H_a^1, \langle \Psi, \Psi \rangle = 1\}. \tag{3}$$

The ground state energy is the most interesting property of an electronic structure. For example, inner atomic forces can be computed from the gradient of E_0 with respect to the variation of the location of the nuclei (Hellman–Feynman forces [48]). Relativistic phenomena have to be treated by the *Dirac equation*. These effects are relevant for heavy atoms and for certain chemical systems. For the sake of simplicity they are mostly neglected or incorporated into the framework of pseudo-potentials.

3. Molecular orbitals in Hartree–Fock model and density functional theory

The subspace $\bigwedge_{i=1}^N L_2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$ of the tensor-product space $L_2((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N) = \bigotimes_{i=1}^N L_2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$ is spanned by determinants of the form

$$\Psi_{SL}(\mathbf{x}_1, s_1; \dots; \mathbf{x}_N, s_N) = \frac{1}{\sqrt{N!}} \det(\varphi_i(\mathbf{x}_j, s_j)), \quad \langle \varphi_i, \varphi_j \rangle = \delta_{i,j},$$

where $\langle \varphi_i, \varphi_j \rangle = \int_{\mathbb{R}^3} \sum_{s=\pm\frac{1}{2}} \varphi_i(\mathbf{x}, s) \overline{\varphi_j(\mathbf{x}, s)} \, d\mathbf{x}$. Such determinants are called *Slater determinants*. A fairly simple approximation is attained by approximating the wave function by a single Slater determinant, $\Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_N, s_N) \approx \Psi_{SL}(\mathbf{x}_1, s_1; \dots; \mathbf{x}_N, s_N)$, as an antisymmetric product of N orthonormal functions $\varphi_i : \mathbb{R}^3 \times \{\pm\frac{1}{2}\} \rightarrow \mathbb{C}$ (respectively \mathbb{R}), $i = 1, \dots, N$, called *orbitals*. It is sufficient to compute real valued orbitals, $\varphi_i(\mathbf{x}) \in \mathbb{R}$. This approximation leads to the well-known *Hartree–Fock model*. For the sake of simplicity we consider in the sequel solely *closed shell systems*. In the *Restricted Closed Shell Hartree–Fock Model* (RHF) one considers pairs of electrons with spin $\pm\frac{1}{2}$. The number of orbitals N will be equal to the number of electron pairs and each orbital depends only on the spatial variable $\mathbf{x} \in \mathbb{R}^3$ [54,30,40].

For reasons of notational convenience we define the so-called *density matrix* $\rho(\mathbf{x}, \mathbf{y}) := \sum_{i=1}^N \varphi_i(\mathbf{x}) \overline{\varphi_i(\mathbf{y})}$ and the *electron density* $n(\mathbf{x}) := 2\rho(\mathbf{x}, \mathbf{x})$.

The energy $E(\Psi_{SL}) = \langle \mathcal{H}\Psi_{SL}, \Psi_{SL} \rangle$ of a single Slater determinant is given by

$$E(\Psi_{SL}) = \sum_{i=1}^N \left[\langle \nabla \varphi_i, \nabla \varphi_i \rangle + \left\langle \left(2\mathcal{V}_{core}(\mathbf{x}) + \mathcal{V}_H(\mathbf{x}) - \frac{1}{2}\mathcal{W} \right) \varphi_i, \varphi_i \right\rangle \right], \tag{4}$$

with the *Hartree potential*

$$\mathcal{V}_H(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{n(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \, d\mathbf{y},$$

satisfying $\Delta \mathcal{V}_H(\mathbf{x}) = -8\pi\rho(\mathbf{x}, \mathbf{x})$, the exchange energy term

$$\mathcal{W}u(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{2\rho(\mathbf{x}, \mathbf{y})}{|\mathbf{x} - \mathbf{y}|} u(\mathbf{y}) \, d\mathbf{y}, \quad \text{and} \quad \mathcal{V}_{core}(\mathbf{x}) = \sum_{j=1}^M \frac{-Z_j}{|\mathbf{x} - \mathbf{R}_j|}.$$

The existence of a minimizer of the Hartree–Fock energy $\Phi = (\varphi_1, \dots, \varphi_N) \mapsto \mathcal{J}_{HF}(\Phi) = E(\Psi_{SL})$ was shown by Lieb and Simon, and improved by P.L. Lions [36,38].

Theorem 1.

- Let $Z := \sum_{j=1}^M Z_j \geq N$, then there exists a minimizer

$$\Phi = \operatorname{argmin} \{ \mathcal{J}_{HF}(\varphi_1, \dots, \varphi_N) : \varphi_i \in H^1(\mathbb{R}^3), \langle \varphi_i, \varphi_j \rangle = \delta_{i,j} \}.$$

- There exists a unitary matrix \mathbf{U} , such that the functions $(\check{\varphi}_i)_{i=1, \dots, N} = \check{\Phi} = \mathbf{U}\Phi$ satisfy the eigenvalue problem

$$\mathcal{H}_\Phi \check{\varphi}_i = \lambda_i \check{\varphi}_i, \quad i = 1, \dots, N, \tag{5}$$

with the Hamiltonian $\mathcal{H}_\Phi = -\frac{1}{2}\Delta + \mathcal{V}_{core} + \mathcal{V}_{H,\Phi} - \frac{1}{2}\mathcal{W}\Phi$.

- The lowest eigenvalues of \mathcal{H}_Φ satisfy $\lambda_1 \leq \lambda_2 \leq \dots \leq \lambda_N < 0$.
- The orbitals are smooth, $\varphi_i \in C^\infty(\mathbb{R}^3 \setminus \{\mathbf{R}_1, \dots, \mathbf{R}_M\})$, and have exponential decay at infinity, $\varphi_i(\mathbf{x}) = \mathcal{O}(e^{-a|\mathbf{x}|})$ if $|\mathbf{x}| \rightarrow \infty, a > 0$.

The property that the minimizer is given by the eigenfunctions corresponding to the lowest N eigenvalues is called the *aufbau principle*. No uniqueness result is known. For $N > 2Z + M$ nonexistence of a minimizer may occur, as shown in [37].

Although the approximation by a single Slater determinant seems to be rather poor, experiences have shown that this approximation is sufficiently good in many situations. Systems for which Hartree–Fock does not provide a sufficient approximation are considered as hard problems in quantum chemistry. Nevertheless, a Hartree–Fock computation is the basis for all post Hartree–Fock methods in quantum chemistry as configuration–interaction, coupled-cluster and perturbation methods [30]. For this reason the Hartree–Fock model is the basic and representative model equation for ab initio methods, which has to be considered in any kind of analysis of the numerical methods used in electronic structure calculations [40]. Furthermore the Hartree–Fock model is a prototype for a variety of equations arising from density functional theory, e.g. the Kohn–Sham equations [46,47].

Density functional theory is based on the observation that the ground state energy E_0 of the electronic Schrödinger equation depends solely on the electron density $\rho(\mathbf{x}, \mathbf{x})$. This result was first distinguished by Kohn and Hohenberg and is known as the *Kohn–Hohenberg theorem* [48,20]. This observation has led to a modification of the Hartree–Fock model,

$$E_{KS}(\Phi) = \sum_{i=1}^N [\langle \nabla \varphi_i, \nabla \varphi_i \rangle + \langle (2\mathcal{V}_{core} + \mathcal{V}_H + \alpha \mathcal{V}_{XC}) \varphi_i, \varphi_i \rangle]. \tag{6}$$

The exchange energy term \mathcal{W} in the Hartree–Fock model, which depends on the full density matrix (not only on the electron density), is replaced by an *exchange correlation potential* $\mathcal{V}_{XC}(\mathbf{x}) = -C_{TF} \rho(\mathbf{x}, \mathbf{x})^{1/3} +$ correction terms. Unfortunately, this potential is not known explicitly. However, many properties of this expression are known, and since it is universal for all electronic systems, there exist successful clues. There is a long list of exchange correlation functionals satisfying the known properties more or less, e.g. LDA, LSD and GGA [20]. These functionals have been proved to be successful in many situations and are widely accepted. In benchmark computations merging between Hartree–Fock and Kohn–Sham equations, so-called hybrid models (e.g. B3LYP, PBE0) of the form

$$E_{HF/KS}(\Phi) = \sum_{i=1}^N \left[\langle \nabla \varphi_i, \nabla \varphi_i \rangle + \left\langle \left(2\mathcal{V}_{core} + \mathcal{V}_H + \alpha \mathcal{V}_{XC} - \frac{1}{2} \beta \mathcal{W} \right) \varphi_i, \varphi_i \right\rangle \right],$$

have been shown to perform best. Here $\alpha = 0$ leads to the Hartree–Fock equations, and $\beta = 0$ to the Kohn–Sham equations in density functional theory. In contrast to Hartree–Fock, where the approximate state function is given

by a Slater determinant built by the orbitals, the orbitals from Kohn–Sham equations are not related to the wave function Ψ . The relevant output quantity is the ground state energy.

The necessary condition for a minimizer $\Phi = (\varphi_1, \dots, \varphi_N)$ of (4) and (6) is cast into an eigenvalue problem of partial differential operators involving a nonlinear operator $\Phi \mapsto \mathcal{G}(\Phi)$

$$\mathcal{H}_\Phi \varphi_i := -\frac{1}{2} \Delta \varphi_i + \mathcal{V}_{core} \varphi_i + \mathcal{G}(\Phi) \varphi_i = \lambda_i \varphi_i, \quad \lambda_1 \leq \dots \leq \lambda_N \leq \lambda_{N+1}.$$

Remarks. Some existence results based on the local density approximation are known also for the Kohn–Sham equations [31]. There several nonlinear terms have been slightly modified to guarantee sufficient regularity for an analytical treatment. Since the correct exchange correlation potential is not known, such modifications may be accepted. Furthermore, since the Kohn–Sham equations are very similar to the Hartree–Fock equations, it is usual practice to assume that the Kohn–Sham system behaves like the Hartree–Fock system. In particular one assumes that the aufbau principle holds.

4. Self consistent field approximation and discretization

An N -tuple $\Phi = (\varphi_1, \dots, \varphi_N)$ of H^1 -functions is called self consistent, or aufbau solution [2], if it satisfies

$$\mathcal{H}_\Phi \varphi_i = \lambda_i \varphi_i, \quad \lambda_1 \leq \dots \leq \lambda_N < \lambda_{N+1}.$$

This relation can be viewed as a fixed point problem and suggests the following iteration scheme for the generation of approximations $\Phi^{(n)} \rightarrow \Phi$, called Roothaan algorithm [34]:

$$\mathcal{H}_{\Phi^{(n)}} \varphi_i^{(n+1)} = \lambda_i^{(n+1)} \varphi_i^{(n+1)}, \quad \lambda_1^{(n+1)} \leq \lambda_2^{(n+1)} \leq \dots \leq \lambda_N^{(n+1)} < \lambda_{N+1}^{(n+1)}. \tag{7}$$

The Roothaan algorithm is a special form of a *self consistent field approximation*. It is important to observe that this linearization of the full nonlinear scheme with N unknown functions decouples completely. The arising linear operator is called *Hamilton–Fock operator*. In particular, for the Kohn–Sham equations the Hamilton–Fock operator has the form of a single particle Schrödinger operator with an external potential $\mathcal{V}(\mathbf{x}) := \mathcal{V}_{core}(\mathbf{x}) + \mathcal{V}_H(\mathbf{x}) + \mathcal{V}_{XC}(\mathbf{x})$. In this respect, the Kohn–Sham equations are simpler than the Hartree–Fock equations because they do not contain a nonlocal operator. It is also important to notice that the Hamilton–Fock operator is defined solely by the density matrix in the Hartree–Fock model, respectively by the electron density in the Kohn–Sham equations.

The solution of the eigenvalue problem (7) can be approximated by well-known numerical methods. Commonly used are Galerkin methods, collocation methods and Finite Differences [3]. The Galerkin scheme has the advantage to be variational, and therefore the numerically computed eigenvalues are always larger as or equal to the exact eigenvalues. Let $\Psi = (\psi_\lambda)_{\lambda \in \mathcal{I}}$ be a Riesz-basis in $L_2(\mathbb{R}^3)$ or in $V_h = \text{span}\{\psi_\lambda : \lambda \in \mathcal{I}\} \subset H^1(\mathbb{R}^3)$ with $\dim V_h < \infty$. For a moment, let us suppose $\Phi^{(n)} = (\varphi_1^{(n)}, \dots, \varphi_N^{(n)})$, $\varphi_i^{(n)} = \sum_{\lambda \in \mathcal{I}} c_{i,\lambda}^{(n)} \psi_\lambda$, to be given. The Galerkin system matrices are given by

$$\begin{aligned} \mathbf{T} &= \left(\frac{1}{2} \langle \nabla \psi_\lambda, \nabla \psi_{\lambda'} \rangle \right), & \mathbf{V}_c &= \left(\langle \mathcal{V}_{core}(\mathbf{x}) \psi_\lambda, \psi_{\lambda'} \rangle \right), \\ \mathbf{V}_H^{(n)} &= \left(\langle \mathcal{V}_H(\mathbf{x}) \psi_\lambda, \psi_{\lambda'} \rangle \right), & \mathbf{W}^{(n)} &= \left(\left\langle \left(-\frac{1}{2} \beta \mathcal{W} + \alpha \mathcal{V}_{XC} \right) \psi_\lambda, \psi_{\lambda'} \right\rangle \right), \end{aligned}$$

which together give the *Hamilton–Fock matrix*

$$\mathbf{H}^{(n)} = \mathbf{H}_{\Phi^{(n)}} = \mathbf{T} + \mathbf{V}_c + \mathbf{V}_H^{(n)} + \mathbf{W}^{(n)}.$$

Once the Hamilton–Fock matrix $\mathbf{H}^{(n)}$ is built, the invariant subspace to the N lowest eigenvalues must be computed. Usually this is done by computing the N eigenvectors $\mathbf{c}_i^{(n+1)}$, $i = 1, \dots, N$, corresponding to the N lowest eigenvalues of $\mathbf{H}^{(n)}$, $\lambda_{1,h}^{(n+1)} \leq \dots \leq \lambda_{N,h}^{(n+1)} < 0$. From these eigenvectors the approximations of the eigenfunctions $\varphi_{i,h}^{(n+1)}$, the density matrix and the electron density can be computed. From the latter quantities one gets the Hamilton–Fock matrix for the next iteration step. Let us remark that this procedure requires at least $\mathcal{O}(N^3)$ arithmetic operations due to the involved diagonalization.

4.1. Basis functions

Different types of trial functions ψ_λ are used in practice.

- (1) Linear combinations of atomic orbitals (LCAO) and Gaussian type orbitals (GTO): Gaussian type basis functions are the traditional basis functions of quantum chemistry. They have the form $\psi_\lambda(\mathbf{x}) = e^{-a_\lambda|\mathbf{R}_j - \mathbf{x}|^2} \times |\mathbf{R}_j - \mathbf{x}|^n Y_{l,m}(\mathbf{R}_j - \mathbf{x})$ where the parameters can be adapted to the atoms of the electronic structure. They have several properties which are highly adapted to the electronic Schrödinger equation, but from the perspective of numerical analysis these basis functions are difficult to analyse. Usually an extremely small number of basis functions \mathcal{N} , abouts 3–20 basis functions per electron, is sufficient even for highly accurate computations. In addition, all matrix elements needed for the computation of the Hartree–Fock model can be calculated analytically. The singularities at the nuclei can be approximated with an exponential rate of convergence with respect to \mathcal{N} [10,32,33,8].
- (2) Plane wave basis sets consist of trigonometric polynomials, $\psi_\lambda(\mathbf{x}) = e^{i\mathbf{k}_\lambda \cdot \mathbf{x}}$, and are used mainly for band structure calculations of crystals. The Coulomb potential with its singularities at the nuclei has to be smoothed by the use of (nonlocal) pseudo potentials. Usually 100–1000 basis functions per atom are then required. In particular, plane wave basis functions are perfectly suited for periodic problems, as they appear in the investigation of crystals.
- (3) In contrast to numerical analysis, local basis functions like finite elements, splines, etc. are only occasionally used. Since there are no boundary conditions involved, finite difference methods, known as grid methods, are mainly used for extremely large molecular systems in conjunction with multigrid methods for the eigenvalue computation. In finite difference schemes and collocation schemes with plane wave bases the potential can be represented by a diagonal matrix in the physical space. A rough estimation shows that about 10^5 – 10^7 basis functions or grid points per atom are required for an all-electron calculation. Using pseudo potentials the number of basis functions per atom may be reduced to 10^3 – 10^6 .

5. Density matrix formulation

To avoid the cubical complexity of the eigenfunction computation, which becomes a bottleneck for solving extremely large systems, one can compute the density matrix [25,27]

$$\rho(\mathbf{x}, \mathbf{y}) := \sum_{i=1}^N \varphi_i(\mathbf{x}) \overline{\varphi_i(\mathbf{y})} = \sum_{i=1}^N \check{\varphi}_i(\mathbf{x}) \overline{\check{\varphi}_i(\mathbf{y})}.$$

Instead of N functions $\varphi_i: \mathbb{R}^3 \rightarrow \mathbb{C}$, we have to compute one function $\rho: \mathbb{R}^6 \rightarrow \mathbb{C}$. This approach is encouraged by the observations, that the Hamilton–Fock operator depends only on the density matrix, $\mathcal{H}_\Phi = \mathcal{H}_\rho$, and that for insulating (nonmetallic) systems the density matrix is known to admit an exponential decay [26]

$$|\rho(\mathbf{x}, \mathbf{y})| \lesssim e^{-\alpha^2|\mathbf{x}-\mathbf{y}|}. \quad (8)$$

Due to this local decay, the discrete approximation of the density matrix can be approximated by $\mathcal{O}(N)$ matrix coefficients. However, this scaling is obtained by considering the ratio of the number of basis functions \mathcal{N} to the number of particles N to be fixed. Methods having this complexity behavior with respect to the number of particles N are called *linear scaling methods* [5,7,26,45,42,52].

Proposition 2. *The operator $\mathcal{P}: u \mapsto \mathcal{P}u(\mathbf{x}) = \int \rho(\mathbf{x}, \mathbf{y})u(\mathbf{y}) \, d\mathbf{y}$ is an orthogonal projection onto $\text{Im } \mathcal{P} = \text{span}\{\varphi_i: 1 \leq i \leq N\}$, i.e., $\mathcal{P}^2 = \mathcal{P}$ and $\mathcal{P}^* = \mathcal{P}$. It has finite rank N and therefore the trace satisfies $\text{Tr } \mathcal{P} = \int \rho(\mathbf{x}, \mathbf{x}) \, d\mathbf{x} = N$.*

In mathematical literature, the projection \mathcal{P} is called a *spectral projection* and ρ the *spectral kernel function* [53].

Proposition 3. *\mathcal{P} and $(-\Delta + 1)^{1/2}\mathcal{P}(-\Delta + 1)^{1/2}$ are Hilbert–Schmidt operators. Furthermore, $\mathcal{P} \in \{A: H^1(\mathbb{R}^3) \rightarrow H^1(\mathbb{R}^3): (-\Delta + 1)^{1/2}A(-\Delta + 1)^{1/2} \in T_0\}$ where T_0 denotes the ideal of trace class operators.*

Proof. The Hartree–Fock ground state energy is $E_{HF} = \int K(\mathbf{x}, \mathbf{x}) \, d\mathbf{x}$, where $K(\mathbf{x}, \mathbf{y}) = [\mathcal{H} - \mathcal{T} - \mathcal{V}_{core}]_{\mathbf{x}} \rho(\mathbf{x}, \mathbf{y})$ is the Schwartz kernel of the operator $(\mathcal{H} - \mathcal{T} - \mathcal{V}_{core})\mathcal{P}$. We conclude that $(-\Delta + 1)^{1/2}\mathcal{P}(-\Delta + 1)^{1/2}$ is in the trace class T_0 and, hence, a Hilbert–Schmidt operator. Moreover, ρ is in $H^1(\mathbb{R}^3) \otimes H^1(\mathbb{R}^3) \subset L_2(\mathbb{R}^3) \otimes L_2(\mathbb{R}^3)$ [53]. \square

According to the Galerkin method, the usual way to approximate ρ is expanding ρ with respect to some orthonormal basis $(\psi_\lambda)_{\lambda \in \mathcal{I}}$ of the finite dimensional trial space $V_h = \text{span}\{\psi_\lambda : \lambda \in \mathcal{I}\} \subset H^1(\mathbb{R}^3)$:

$$\rho(\mathbf{x}, \mathbf{y}) \approx \rho_h(\mathbf{x}, \mathbf{y}) = \sum_{\lambda, \lambda'} p_{\lambda, \lambda'} \psi_\lambda(\mathbf{x}) \psi_{\lambda'}(\mathbf{y}).$$

The coefficients $p_{\lambda, \lambda'}$ form the stiffness matrix

$$\mathbf{P} = (p_{\lambda, \lambda'})_{\lambda, \lambda' \in \mathcal{I}} = ((\mathcal{P}\psi_{\lambda'}, \psi_\lambda))_{\lambda, \lambda' \in \mathcal{I}}$$

of the operator \mathcal{P} with respect to the basis $(\psi_\lambda)_{\lambda \in \mathcal{I}}$.

Assumption A. We suppose there is a gap between the N th and $(N + 1)$ st eigenvalue of \mathcal{H} , i.e. there exists a number μ with $\lambda_N < \mu < \lambda_{N+1}$. Due to the known convergence of the Galerkin scheme, for a sufficiently large trial space $V_h \subset H^1(\mathbb{R}^3)$ the number of negative eigenvalues of $\mathbf{H}' := \mathbf{H} - \mu\mathbf{I}$ is N .

Proposition 4. Under the above assumptions the matrix \mathbf{P} satisfies the following assertions

- (1) $\mathbf{P}^2 = \mathbf{P}$, $[\mathbf{P}, \mathbf{H}] = [\mathbf{P}, \mathbf{H}'] = 0$,
- (2) $\mathbf{P}^* = \mathbf{P}$, $\mathbf{P} \geq 0$, $\dim \text{Im } \mathbf{P} = \text{Tr } \mathbf{P} = N$,
- (3) $\sum_{i=1}^N \lambda_{i,h} = \langle \langle \mathbf{P}, \mathbf{H} \rangle \rangle := \sum_{\lambda, \lambda' \in \mathcal{I}} p_{\lambda, \lambda'} h_{\lambda, \lambda'} = \text{Tr}(\mathbf{P}\mathbf{H}) = \text{Tr}(\mathcal{P}_h \mathcal{H}_h)$,
- (4) $\mathbf{P} = \text{argmin}\{\text{Tr}(\mathbf{P}\mathbf{H}) : \mathbf{P}^2 = \mathbf{P}, \mathbf{P}^* = \mathbf{P}, \text{Tr } \mathbf{P} = N\}$.

To obtain linear scaling w.r.t. N , one may compute \mathbf{P} respectively $\rho_h(\mathbf{x}, \mathbf{y})$ instead of $\varphi_{i,h}$, $i = 1, \dots, N$ [26,27].

5.1. Matrix-sign function method

The discrete density matrix \mathbf{P} satisfies

$$\mathbf{P} = (p_{\lambda, \lambda'}) = \frac{1}{2}(\mathbf{I} - \text{sign}(\mathbf{H} - \mu\mathbf{I}))$$

with the *matrix-sign function* $\text{sign}(\mathbf{A})$ of a symmetric matrix \mathbf{A} . The matrix $\mathbf{S} := \text{sign}(\mathbf{A})$ can be obtained by various iteration procedures, $\mathbf{S}_k \rightarrow \mathbf{S}$, e.g. the Newton–Schultz iteration (*) and the Newton iteration (+):

$$\mathbf{S}_0 = \mathbf{A} / \|\mathbf{A}\|, \quad \mathbf{S}_{n+1} = \frac{1}{2}(3\mathbf{S}_n - \mathbf{S}_n^3), \tag{*}$$

or

$$\mathbf{S}_{n+1} = \frac{1}{2}(\mathbf{S}_n + \mathbf{S}_n^{-1}). \tag{+}$$

Proposition 5. In order to get an approximation of \mathbf{S} with an accuracy ε one needs $n_{it} \sim \log \kappa + \log \log(1/\varepsilon)$ steps of the Newton–Schultz iteration where $\kappa = \text{cond}_2(\mathbf{H}')$.

Proof. Diagonalization of $\mathbf{S}_0 = \mathbf{V}^T \mathbf{D} \mathbf{V}$, with $\mathbf{D} = \text{diag}(\lambda_i)$, yields the \mathcal{N} simultaneous iterations

$$\lambda_i^{(n+1)} = \frac{1}{2}(3\lambda_i^{(n)} - (\lambda_i^{(n)})^3), \quad i = 1, \dots, \mathcal{N},$$

each of them converging to one of the fixed points $-1, 0, 1$. It can be seen that one needs $\mathcal{O}(\log |\frac{\lambda_{\max}}{\lambda_i}|)$ iterations to obtain an accuracy ε (if $\lambda_i \neq 0$). Moreover for sufficiently small $|\lambda_i^{(\infty)} - \lambda_i^{(n)}|$ there holds $|\lambda_i^{(\infty)} - \lambda_i^{(n+1)}| \lesssim 3|\lambda_i^{(\infty)} - \lambda_i^{(n)}|^2$. To obtain an accuracy ε , one needs $\mathcal{O}(\log \log(1/\varepsilon))$ iterations. \square

Due to the quadratic convergence, the Newton–Schultz iteration is probably the most efficient method for computing the matrix \mathbf{P} . Approximations of matrix–matrix-multiplication schemes introduce an additional error which can accumulate in the iteration procedure.

5.2. Cauchy–Dunford integral method

The orthogonal projector \mathbf{P} has an integral representation:

$$\mathbf{P} = -\frac{1}{2\pi i} \int_{\Gamma_-} (\mathbf{H}' - z\mathbf{I})^{-1} dz$$

where $\Gamma_- \subset \mathbb{C}$ is a closed curve with positive orientation surrounding $\sigma_- = \{\lambda_{1,h} - \mu, \dots, \lambda_{N,h} - \mu\}$. This contour integral may be discretized by the trapezoidal rule providing exponential convergence w.r.t. the number of quadrature points [23]. The inversion of $\mathbf{H}' - z\mathbf{I}$ can be performed iteratively. Moreover, an appropriate pre-conditioner of the operators $\mathbf{H}' - z\mathbf{I}$ can be used, e.g. multi-level methods [15,28].

5.3. Purification functional optimization

As we have already observed, the matrix \mathbf{P} is the unique solution of the following optimization problem:

Problem A. Find $\mathbf{P} \in \mathbb{R}^{\mathcal{N} \times \mathcal{N}}$, $\mathbf{P}^* = \mathbf{P}$, that minimizes

$$E(\mathbf{P}) = \text{Tr}(\mathbf{P}\mathbf{H}'),$$

subject to the constraints $\mathbf{P}^2 = \mathbf{P}$ and $\text{Tr} \mathbf{P} = N$.

Solving Problem A by standard optimization tools is difficult because of the constraints $\mathbf{P}^2 = \mathbf{P}$ and $\text{Tr} \mathbf{P} = N$. In order to get rid of these constraints, the authors in [35] have introduced a modified optimization problem without constraint conditions.

Problem B. Find $\mathbf{P} \in \mathbb{R}^{\mathcal{N} \times \mathcal{N}}$, $\mathbf{P}^* = \mathbf{P}$, that minimizes

$$J_B = J_B(\mathbf{P}) = \text{Tr}(3\mathbf{P}^2 - 2\mathbf{P}^3)\mathbf{H}'.$$

Lemma 6. A local minimum \mathbf{P} of Problem B is a stationary point of J_B ; i.e. \mathbf{P} satisfies

$$J'_B(\mathbf{P}) = 3(\mathbf{P}\mathbf{H}' + \mathbf{H}'\mathbf{P}) - 2(\mathbf{P}^2\mathbf{H}' + \mathbf{P}\mathbf{H}'\mathbf{P} + \mathbf{H}'\mathbf{P}^2) = 0.$$

Theorem 7. Problem B has exactly one local solution $\mathbf{P} \in \mathbb{R}^{\mathcal{N} \times \mathcal{N}}$ which coincides with the solution of Problem A. This solution satisfies $\mathbf{P} \geq 0$.

The minimisation, i.e. the computation of the (local) solution of Problem B, can be performed by gradient, respectively conjugate gradient methods using J'_B . For the conjugate gradient method, the number of iterations is expected to be roughly $n_{it} \sim \sqrt{\kappa}$ provided that the initial approximation is inside a sufficiently small environment of \mathbf{P} . This method can also be used in combination with the sign function iteration.

6. Multi-resolution analysis and wavelet bases

Multi-resolution analysis and wavelet bases are recent tools for efficient approximations of functions [17,39,12,24]. Instead of a single and fixed trial space V_h for the discretization, we consider a nested sequence of spaces $V_j = \text{span}\{\phi_{j,k}: k \in \Delta_j\}$ whose union is dense in $L^2(\mathbb{R})$,

$$(V_{-l} \subset V_{-l+1} \subset \dots) V_0 \subset V_1 \subset \dots \subset V_j \subset V_{j+1} \subset \dots \subset L^2(\mathbb{R}).$$

In the stationary setting of multi-resolution analysis [39], the basis functions $\phi_{j,k}$ are generated by a single scaling function, e.g. ϕ by $\phi_{j,k}(x) = 2^{j/2}\phi(2^j x - k)$, $x \in \mathbb{R}$. The scaling functions should be local, $\text{diam supp } \phi_{j,k} \sim 2^{-j}$.

Then the generating function ϕ has compact support. In this case ϕ has only finite regularity $\gamma := \sup\{s \in \mathbb{R} : \phi \in H^s(\mathbb{R})\}$. For the sake of simplicity, we consider orthogonal basis functions in the present paper, $\langle \phi_{j,k}, \phi_{j,k'} \rangle = \delta_{k,k'}$.

Since $V_j \subset V_{j+1}$ one can decompose

$$V_{j+1} = V_j \oplus W_j, \quad V_J = \bigoplus_{j=-1}^{J-1} W_j, \quad W_{-1} := V_0$$

with appropriate complementary spaces W_j , $V_j \cap W_j = \{0\}$. The corresponding basis functions $\psi_{j,k}$, spanning

$$W_j = \text{span}\{\psi_\lambda : \lambda = (j, k), k \in \nabla_j := \Delta_{j+1} \setminus \Delta_j\},$$

should be local with respect to the corresponding scale $j = |\lambda|$

$$\text{diam supp } \psi_{j,k} \sim 2^{-j}, \quad \text{diam supp } \phi_{j,k} \sim 2^{-j}.$$

In the stationary setting in \mathbb{R} , there is also a compactly supported function ψ such that $\psi_{j,k}(x) = 2^{j/2}\psi(2^j x - k)$, $x \in \mathbb{R}$. If one considers orthogonal basis functions these basis functions satisfy $\langle \psi_{j,k}, \psi_{j',k'} \rangle = \delta_{(j,k),(j',k')}$. A very important property of wavelet bases is that they are orthogonal to all polynomials up to a degree $d - 1$, i.e. orthogonal wavelet bases have d vanishing moments

$$|\langle \psi_{j,k}, x^\alpha \rangle| = 0, \quad 0 \leq \alpha < d.$$

The orthogonality condition is very restrictive. In general one considers biorthogonal wavelet bases. Perhaps orthogonality simplifies the numerical solution of eigenvalue problems since the Gramian matrix is simply the identity matrix. But we do not go into further detail. There are three mother wavelets in \mathbb{R}^2 , which can be built by tensor-products, $\psi_{1,0}(x, y) = \psi(x)\phi(y)$, $\psi_{0,1}(x, y) = \phi(x)\psi(y)$, $\psi_{1,1}(x, y) = \psi(x)\psi(y)$. Isotropic wavelets in higher dimensions are constructed analogously.

One of the most intriguing properties of wavelets are the norm equivalences [19,12,15,16].

Theorem 8. For $|s| < \gamma$ the Sobolev norms $\|\cdot\|_s$ of Sobolev spaces $H^s(\mathbb{R}^n)$ can be expressed by the wavelet expansion

$$\|u\|_s^2 \sim \sum_{\lambda} |\langle u, \psi_\lambda \rangle|^2 2^{2|\lambda|s}.$$

For $s = \frac{n}{p} - \frac{n}{2}$ ($s = \frac{1}{p} - \frac{1}{2}$ in 1D), $|s| < \gamma$ the Besov norm of u can be expressed by

$$\|u\|_{B_{p,p}^s}^p \sim \sum_{\lambda} q |\langle u, \psi_\lambda \rangle|^p.$$

7. Best \mathcal{N} -term approximation

Let us consider a Riesz Basis $\Psi = (\psi_\lambda)_{\lambda \in \mathcal{I}}$ in some Hilbert space H . For $v \in H$, we consider the error of the best \mathcal{N} -term approximation

$$\sigma_{\mathcal{N},H,\Psi}(v) = \min \left\{ \left\| v - \sum_{\lambda \in \mathcal{T}} w_\lambda \psi_\lambda \right\| : w_\lambda \in \mathbb{C}, \mathcal{T} \subset \mathcal{I}, \#\mathcal{T} = \mathcal{N} \right\}.$$

The space of all functions permitting a best \mathcal{N} -term approximation up to an accuracy $\varepsilon = \mathcal{N}^{-s}$, $A^s(H, \Psi) := \{v \in H : \sigma_{\mathcal{N},H,\Psi}(v) \lesssim \mathcal{N}^{-s}\}$, is a quasi-normed space equipped with the quasi-norm $\|v\|_{A^s} := \sup_{n \in \mathbb{N}} n^s \sigma_{n,H,\Psi}(v) + \|v\|$.

An immediate consequence of Theorem 8 is that the convergence of functions u in the energy space $H = H^1(\mathbb{R}^3)$ can be transformed into an approximation problem in the sequence space $l_2(\mathcal{I})$. Expanding $v \in H$ with respect to the Riesz basis Ψ , $v = \mathbf{v}^T \Psi = \sum_{\lambda \in \mathcal{I}} v_\lambda \psi_\lambda$, the norms $\|v\|$ and $\|\mathbf{v}\|_{l_2(\mathcal{I})}$ are equivalent. This allows to consider the space of vectors $\mathbf{v} \in l_2(\mathcal{I})$ instead of $v \in H$. Let $\mathbf{v}^* = (v_k^*)_{k \in \mathbb{N}}$ be a rearrangement of \mathbf{v} with respect to decreasing order, i.e. $|v_k^*| \geq |v_{k+1}^*|$. Obviously, the best n -term approximation of \mathbf{v}^* is $\mathbf{v}_n^* := (v_1^*, \dots, v_n^*, 0, \dots)$ and $\sigma_{n,l_2(\mathcal{I})} = \|\mathbf{v}^* - \mathbf{v}_n^*\|_{l_2(\mathcal{I})} = (\sum_{k>n} |v_k^*|^2)^{1/2}$. For $0 < \tau \leq 2$, we define the weak l_τ -norm of \mathbf{v} by

$$\|\mathbf{v}\|_{l_\tau^w} := \|\mathbf{v}\|_{l_2} + |\mathbf{v}|_{l_\tau^w}, \quad |\mathbf{v}|_{l_\tau^w} := \sup_{k \in \mathbb{N}} |v_k| k^{1/\tau}. \tag{9}$$

Theorem 9. [13] *If $s = \frac{1}{\tau} - \frac{1}{2}$ then the space A^s can be characterized by the weak l_τ space $\|v\|_{A^s} \sim \|\mathbf{v}\|_{l_\tau^w}$. Moreover, for any $\varepsilon > 0$ there holds $\|\mathbf{v}\|_{l_{\tau+\varepsilon}(\mathcal{I})} \lesssim \|\mathbf{v}\|_{l_\tau^w} \lesssim \|\mathbf{v}\|_{l_\tau(\mathcal{I})}$. Remarkably, $\|\mathbf{v}\|_{l_\tau(\mathcal{I})} \sim \|v\|_{B_{\tau,\tau}^{s/n}(\mathbb{R}^n)}$, if $\mathbf{H} = L_2(\mathbb{R}^n)$ and Ψ is a wavelet basis.*

7.1. Tensor-product bases and sparse grid

So far we have dealt only with isotropic wavelet bases in higher dimensions, where $\text{diam supp } \psi_\lambda \sim 2^{-|\lambda|}$. There is an alternative way for introducing multi-scale bases by a tensor product construction, $\psi_{\lambda_1, \lambda_2} = \psi_{\lambda_1}(\mathbf{x})\psi_{\lambda_2}(\mathbf{y})$. This tensor product basis $\Psi \otimes \Psi := (\psi_{\lambda, \lambda'}(\mathbf{y}))_{\lambda, \lambda' \in \mathcal{I}}$ is a Riesz basis in $\mathbf{H} \otimes \mathbf{H}$. The best \mathcal{N} -term approximation w.r.t. this basis gives the *sparse grid* or *hyperbolic cross approximation*, known as a versatile tool for approximation in \mathbb{R}^n , $n > 1$, cf. [9,44,59].

Theorem 10. [44] *The quasi-Banach spaces $l_p(\mathcal{I})$, $0 < p \leq 2$, $\mathcal{I} = \mathbb{Z}^n$ are tensor product spaces*

$$l_p(\mathbb{Z}^n) = \bigotimes_{i=1}^n l_p(\mathbb{Z}).$$

This means that a function in $\bigotimes_{i=1}^n B_{\tau,\tau}^s(\mathbb{R})$ can be approximated with convergence rate \mathcal{N}^{-s} regardless of the number \mathcal{N} of degrees of freedom to discretize the orbitals φ_i . Only the constants in the norm equivalence are growing exponentially, like C^n with dimension n . We remark that the assertion of Theorem 10 is not true for weak $l_\tau(\mathcal{I})$ spaces, where one has to include additional logarithmic terms like $(\log \mathcal{N})^n$. The following theorems [21] show the regularity of the orbitals φ and density matrices ρ stemming from the Hartree–Fock model. Similar results hold in H^1 instead of L_2 .

Theorem 11. [22] *For every $s > 0$ the density matrix ρ belongs to $B_{p,p}^s(\mathbb{R}^3) \otimes B_{p,p}^s(\mathbb{R}^3)$ whenever p and s are related by $s = \frac{3}{p} - \frac{3}{2}$. Furthermore the density matrix \mathbf{P} discretized by the Galerkin method using (isotropic) wavelets Ψ is in $l_p(\mathcal{I}) \otimes l_p(\mathcal{I})$ if the number of vanishing moments d satisfies $d > s$.*

Theorem 12. [22] *For every $s > 0$, there holds $\varphi_j \in \bigotimes_{i=1}^3 B_{\tau,\tau}^s(\mathbb{R})$ and $\rho \in \bigotimes_{i=1}^6 B_{\tau,\tau}^s(\mathbb{R})$ whenever τ and s are related by $s = \frac{1}{\tau} - \frac{1}{2}$. The wavelet coefficients of the orbitals φ_j and the density matrix satisfy $(\langle \varphi_j, \bigotimes_{i=1}^3 \psi_{\lambda_i} \rangle) \in l_\tau(\mathcal{I})$ and $(\langle \rho, \bigotimes_{i=1}^6 \psi_{\lambda_i} \rangle) \in l_\tau(\mathcal{I}^2)$ if the number of vanishing moments d satisfies $d > s$.*

As a consequence the best \mathcal{N} -term approximation converges with rate \mathcal{N}^{-s} , $s < d$. I.e. the approximation in \mathbb{R}^6 scales as an approximation in \mathbb{R} . This would reduce the number of basis functions again by a substantial portion.

The above estimates do not consider the dependence w.r.t. N directly. We remark that the prefactor of \mathcal{N}^{-s} is bounded by the mixed Besov-norm of the density matrix, which depends on the number of particles N . Under the assumption that this norm is growing at most linearly with respect to the number of atoms respectively electrons N , we obtain for a fixed relative approximation error that the number of nonzero coefficients representing the density matrix grows linearly with N . If we fix the number of particles, then the complexity is still $\mathcal{O}(\mathcal{N})$. Indeed, this is a much better scaling as obtained by previous linear scaling methods. The above assumption is obviously satisfied for M independent systems and is in general quite reasonable. However, it is not completely satisfied for the free electron gas. We still expect a reasonable efficiency also for metallic systems.

8. Operator algebra

It remains to demonstrate that the discretization as well as all iterates can be computed with (almost) linear cost. Since we do not know the speed of convergence of the self consistent field iteration, our considerations are confined to one single iteration step. The following techniques provide sparse data representations for the operators under consideration. They contain the original Hamilton–Fock matrix, as well as the final density matrix. Additionally, they are matrix algebras, closed with respect to linear combinations and matrix–matrix products.

- \mathcal{H} -matrices [6],
- wavelet matrix compression [4,14,49],
- Kronecker product approximation [58,57,5].

Indeed, operators $A : H^t(\mathbb{R}^3) \rightarrow H^{-t}(\mathbb{R}^3)$ with a Schwartz kernel satisfying a Calderón–Zygmund type estimate [41,55]

$$|\partial_{\mathbf{x}}^\alpha \partial_{\mathbf{y}}^\beta K(\mathbf{x}, \mathbf{y})| \lesssim \frac{1}{|\mathbf{x} - \mathbf{y}|^{3+2t+|\alpha|+|\beta|}}, \quad \mathbf{x} \neq \mathbf{y},$$

have matrix coefficients

$$2^{-t(l+l')} |\langle \psi_\lambda, A\psi_{\lambda'} \rangle| \leq C \frac{2^{-|l-l'|(3/2+\sigma)}}{(1 + 2^{\min(l,l')} \text{dist}(\text{supp } \psi_\lambda, \text{supp } \psi_{\lambda'}))^{3+\beta}} \tag{10}$$

where $\sigma > 0$, $\beta + 3 = 2d$ and d denotes the number of vanishing moments of the wavelets ψ_λ . Such matrices are *compressible*, since they can be approximated by sparse matrices [14,12,56]. Lemarie has shown that the class of compressible matrices is closed w.r.t. composition [56]. This means that the product of two compressible matrices is again compressible. Similar algebraic structures are known for hierarchical [6] and Kronecker product matrices.

Proposition 13. [22] *The projection operator $\mathcal{P} : H^1(\mathbb{R}^3) \rightarrow H^{-1}(\mathbb{R}^3)$ defined by the density matrix admits a sparse matrix approximation \mathbf{P}_ε with $\mathcal{O}(\mathcal{N})$ nonzero matrix entries.*

Requiring the error of procedure to be lower than the error of discretization $\varepsilon \sim \mathcal{N}^{-s}$, the approximation procedures for computing the density matrix (Section 5) need $n_{it/quad} = \mathcal{O}(|\log \varepsilon|^\alpha) = \mathcal{O}((\log \mathcal{N})^\alpha)$ iteration steps and quadrature nodes, respectively. All iterates are compressible. Estimating the constants in (10) by $C_{(n_{it/quad})} \lesssim C_{(0)}^{n_{it/quad}} \sim C_{(0)}^{(\log \mathcal{N})^\alpha}$ is far too pessimistic, since by Proposition 13 the resulting density matrix is sparse. Therefore the computation of the density matrix can be performed within a linear, or almost linear cost w.r.t. to the number of basis functions \mathcal{N} .

9. Numerical experiments

In this section we present some numerical experiments showing the behavior of the methods for computing the discrete density matrix \mathbf{P} presented in Section 5. We replace the linear eigenvalue problem (7) by the simplest one-dimensional periodic analogue,

$$-\frac{1}{2} \Delta \varphi_i = \lambda_i \varphi_i, \quad \varphi_i \in H_{per}^1(0, 1),$$

and seek for $\rho(x, y) = \sum_{i=0}^N \varphi_i(x) \varphi_i(y)$, where $\varphi_0, \dots, \varphi_N$ are the L_2 -normalized eigenfunctions to the $N + 1$ lowest eigenvalues. For the Galerkin discretization we choose V_J as trial space and use its wavelet basis [1,25,18,29,34]. The corresponding discrete density matrix \mathbf{P} is quasi-sparse, i.e. it can be compressed to a sparse matrix. Specifying the parameters, we set $N = 30$ and $J = 9$ which corresponds to $\dim V_J = 512$. In this way we get a discretization error of $E_{dis} = (\text{Tr}(\mathbf{P}\mathbf{H}) - \sigma) / \sigma \approx 3.7 \times 10^{-7}$ where $\sigma = \sum_{i=0}^N \lambda_i$.

Firstly, we study the behavior of the matrix-sign function method in the special case of the Newton–Schultz iteration using approximations for fast matrix multiplications. We compute the approximation \mathbf{P}_{appr} of \mathbf{P} without a truncation and with two truncation methods, H1 and H1H, applied to the Newton–Schultz iterates and to the intermediate matrices after each matrix multiplication. Both of them are based on the norm equivalence

$$\|\rho\|_{H_{per}^1 \otimes H_{per}^1}^2 \sim \sum_{j_1, j_2} \sum_{k_1, k_2} 2^{2(j_1+j_2)} |\langle \rho, (\psi_{j_1, k_1})^{per} \otimes (\psi_{j_2, k_2})^{per} \rangle|^2,$$

whereas H1H additionally keeps matrix entries corresponding to the pattern of the Hamilton–Fock matrix. We never exceeded the population of the Hamilton–Fock matrix (see Fig. 1). Secondly, we demonstrate the behavior of the Cauchy–Dunford integral method. We approximate the Cauchy–Dunford integral by the trapezoidal rule with n_{quad}

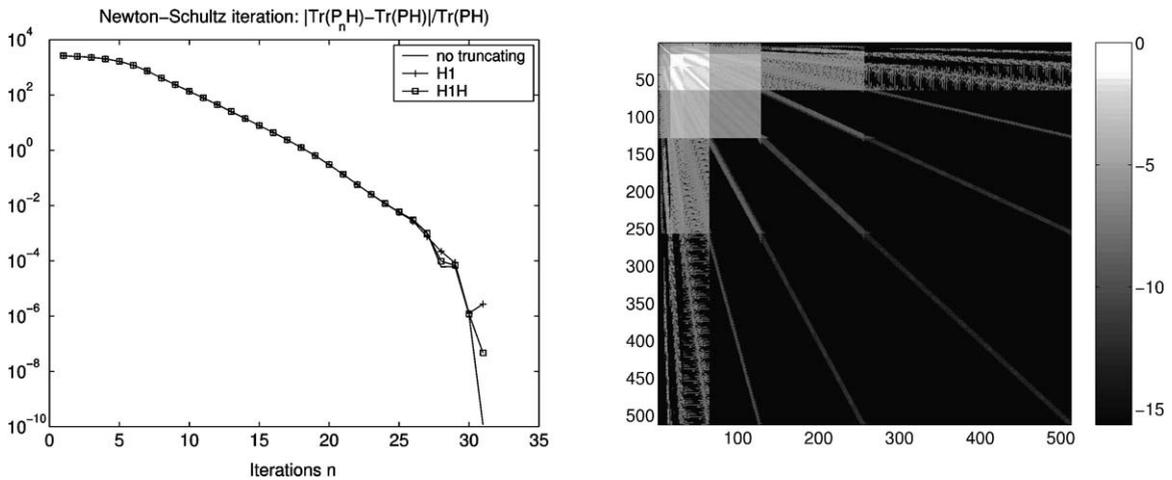


Fig. 1. Errors of truncated Newton–Schultz iteration and structure of resulting approximation \mathbf{P}_{appr} in case of H1H-truncating.

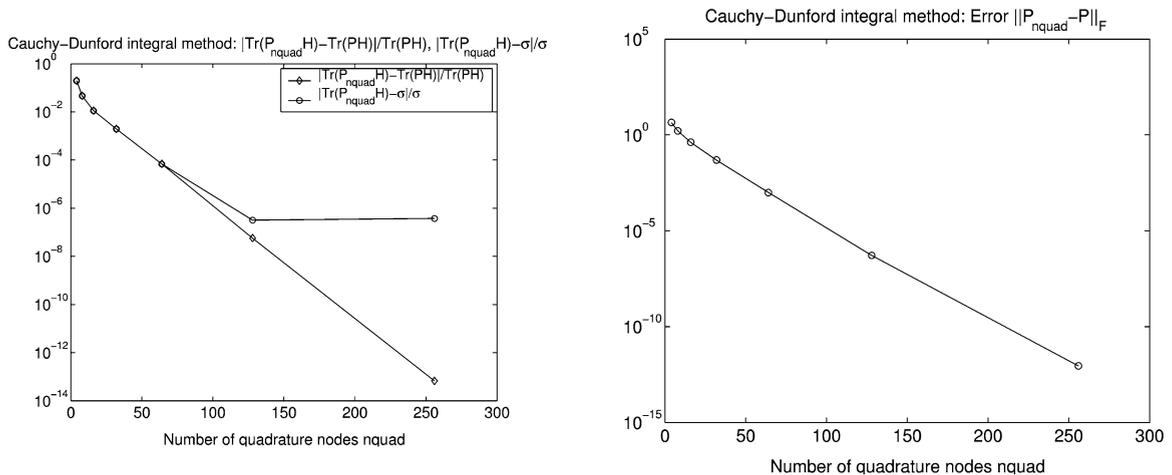


Fig. 2. Errors of approximate Cauchy–Dunford integral.

equidistant quadrature nodes (see Fig.2). Finally, we apply several optimization algorithms performing the purification functional optimization (see Fig. 3). We consider the steepest descent method with exact line searches and the nonlinear conjugate gradient methods Fletcher–Reeves, Polak–Ribière and Polak–Ribière with restarts, all of them with exact line searches.

10. Conclusion

Even if the above toy problems are far from realistic simulations several conclusions can be drawn. All methods are computing the compressed discrete density matrix in a reasonable number of iteration steps accurately. All these methods allow fast matrix operations, provided by wavelet and hierarchical matrix compression, without deteriorating the reliability. Reasonable compression can be obtained even for metallic systems. However, we do not claim linear complexity in this setting.

The most efficient method seems to be the Newton–Schultz iteration. Since each iteration step is only approximately performed we do not have sufficient error control. In contrast, the gradient of the purification functional controls the error. The efficiency of the minimization algorithms hopefully may be improved by proper preconditioning. Even the combination of both methods seems to be appropriate.

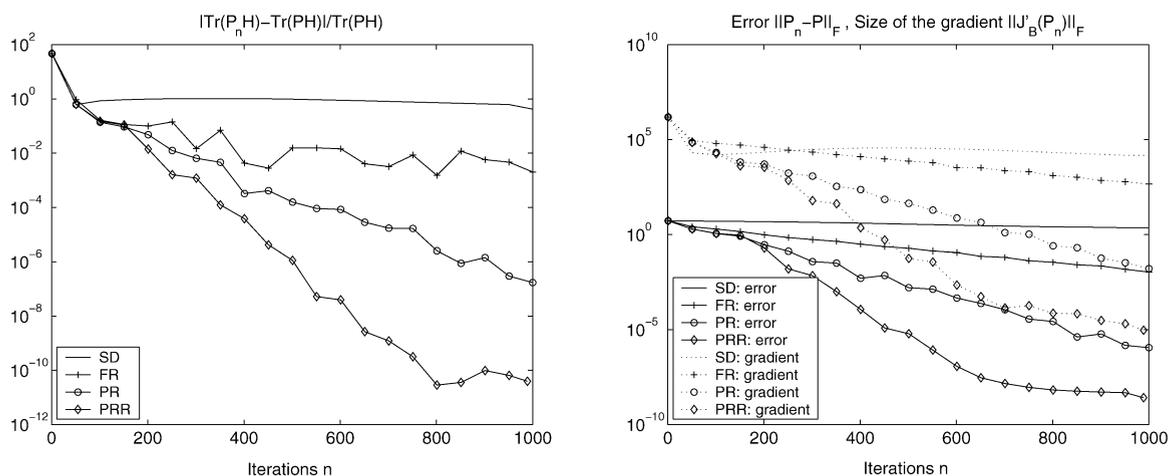


Fig. 3. Errors and gradient sizes of purification functional optimization (SD: steepest descent, FR: Fletcher–Reeves, PR: Polak–Ribière, PRR: Polak–Ribière with restarts).

The Cauchy–Dunford integral method has the advantage that it does not require the Hamilton–Fock matrix explicitly. Already matrix–vector multiplications are sufficient to compute the columns of the density matrix. For parallel as well as for adaptive computations this method becomes highly attractive.

The advantage of wavelet bases comes mainly from two reasons. The hyperbolic cross approximation can relieve the curse of dimensions and the concept of adaptivity may further reduce the required number of basis functions substantially. Probably the ratio of the number of particles to the number of basis functions still will be much larger than for standard GTO basis sets. However, due to linear scaling the proposed methods provide a perspective for electronic structure computation up to the modeling errors of density functional theory, even for extremely large systems and transition metals.

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