Wavelet Based Density Operators, 
Electron Density and Energy Functionals

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Introduction

Advances in computational technology opened up new opportunities in quantum mechanical calculation of various electronic structures, like molecules, crystals, surfaces, mesoscopic systems, etc. The calculations can only be carried out either for very limited systems or with restricted models, because of their great demand of computational and data storage resources. Independent particle approximations, like the Hartree–Fock based [1]–[4] algorithms with single determinant wave functions, leave out the electron correlation and need operation and storage capacity of order \( N^4 \), if \( N \) is the total number of electrons in the system. If inclusion of the electron correlation is necessary, configuration interaction (CI) or coupled cluster (CC) methods can be applied, with very high demand of computational resources (\( O(N^6) \) to \( O(\exp N) \)). An alternative way is to use perturbation theory (PT). The second order perturbation calculations can be carried out within quite reasonable time and resource limits, but the results are usually unsatisfactory, they just show the tendencies, while the 4th order PT needs \( O(N^7) \) to \( O(N^8) \) operations. All these algorithms use the \( N \)-electron wave function as a basic quantity.

Another branch of methods use electron density as the primary entity. Pioneers of this trend, like Thomas [5], Fermi [6], [7], Frenkel [8] and Sommerfeld [9] developed the statistical theory of atoms and the local density approximation. The space around the nuclei is separated into small regions, where the atomic potential is approximated as a constant, and the electrons are modeled as a free electron gas of Fermi–Dirac statistics [10]–[12]. Dirac included electron correlation [13], which improved the results.

After the Hohenberg–Kohn theorems had appeared [14], and Kohn and Sham had offered a practically applicable method [15] based on their work, many scientists were motivated to work on the theory, and it developed into one of the most powerful electron calculating methods.

The Hungarian traditions of density based electron structure calculations are also noteworthy [16]. Gombás and his group have improved the statistical theory of atoms [17], and suggested pseudopotentials for it [18], Gáspár introduced one of the fundamental exchange-correlation potentials [19].

Despite the success of density functional theory, it has some drawbacks.
The exact formula of the exchange-correlation potential is not known, thus chemical intuition and measured data are necessary in order to approximate it, and the kinetic energy functional is hard to calculate. Powerful approximating formulas are available (see, e.g. [20]), like the Thomas–Fermi functional based gradient and generalized gradient expansions, where the energy functionals are expressed as a power series of the gradient of the density (the first such suggestion was [21]). A similar method, based on locally linear potential of the Airy gas also exists [22]–[24]. The method is referred as the local Airy gas approximation or edge electron gas, because quickly varying, almost linear potentials appear typically at surfaces.

Considering the historical development of sophisticated $N$-electron methods, a typical trend can be observed. Starting with a very simple model, new details are introduced in order to improve the results. This scheme is followed in the linear muffin tin orbital method [25] where the plane wave approximation in the interatomic regions is replaced by an atomic potential around the nuclei. Similarly, the linearized augmented plane wave method [26] and the plane wave pseudopotential approach [27] describe the details of the crystal potential differently in different spatial regions. Although they are rather successful, for applying any of these models, chemical intuition is needed, free parameters, like the radius of the bordering sphere between the two types of potentials, and the boundary conditions have to be set. A systematic method, which can handle the different behaviors of the electron structures at different spatial domains, or either at different length scale [28], is required. Multiresolution or wavelet analysis, this rapidly developing branch of the applied mathematics, is exactly the tool for such purposes.

From mathematical point of view multiresolution analysis (MRA) is a theory of a special kind of Hilbert space basis sets. Basis sets are commonly used in all electron structure calculations, as the wave function is usually expanded as linear combination of some kind of basis functions. Thus the operator eigenvalue problem is reduced to an algebraic matrix eigenvector problem. The resulting algebraic equations are easier to solve, well known algorithms and subroutine libraries are available, however, the difficulty of choosing the proper basis set arises. If linear combination of atomic orbitals (LCAO) is used, the atomic basis functions are Slater or Gaussian-type of functions [29], [30], the selection of atomic orbitals needs chemical intuition, which is a result of long time’s experience, and can not be algorithmized. Both basis sets are non-orthogonal, and lack the explicit convergence properties [31]. Moreover, calculation of operator matrix elements with Slater-type orbitals is complicated, their integrals have to be treated numerically. Although integrals of Gaussian functions are analytically known, the Gaussian-type basis does not reflect the nuclear cusp condition of Kato. He published his cusp conditions [32], which reflects on singularities of the $N$-electron wave function in the presence of Coulomb-like potentials. Since then it turned out that for high precision numerical calculations it is essential to satisfy these
requirements. However, while the nuclear cusp condition is relatively easy to fulfill by Slater-type orbitals, the electron-electron cusp is extremely hard to represent.

In solid state physics, where more or less periodic systems are studied, choosing plane wave basis sets is rather usual. These basis functions are system independent and easily computable, but the results are not always convincing and the number of necessary basis functions is almost untreatable. (Theoretically, plane waves could also be used for describing molecules, since the two-electron integrals and the expectation values are connected to the Fourier transform, thus they are easily computable, and this could balance the large number of necessary basis functions.) The reason, why so many plane waves are needed is that the wave functions around the nuclei need very high frequency terms, i.e. high resolution level, for reproducing the nuclear cusps. In the framework of Fourier analysis, the whole space has to be expanded at the same resolution, despite that in most of the space low frequency terms would be sufficient.

Multiresolution analysis offers the possibility to handle the functions locally with different resolution, thus many unnecessary calculations can be spared by adapting the refinement level to the actual electron system. Wavelets, the basis elements of MRA, are localized functions, they are generated by dilations and translations from one common mother wavelet, all of them are similar, and they can be used as simple building blocks in expansion of functions. Because of their generation, they can well describe features of different scales and positions simultaneously. Based on the multiresolution analysis, both the nuclear cusp of the density and the electron-electron cusp condition of the two-electron density matrix can be represented by an MRA expansion of the density matrices.

In the dissertation I am going to summarize our experiences about wavelet-type basis functions and their application possibilities. In the first chapter the wavelets and multiresolution analysis are defined, based on the work of Daubechies [33], Chui [34], Heil and Walnut [35]. In Chapter 2 some properties of the density matrices, the reduction of degrees of freedom and the contracted density matrices are mentioned and the notations we used are fixed. In the next chapter Kato’s cusp conditions will be presented, which have played essential role in our works. The train of thought by Bingel is followed in adapting the conditions for density matrices. In Chapter 4 first the Hohenberg–Kohn theorems and the \( \nu \)-representability problem will be presented briefly, based on [20] and [16], then extensions of the Hohenberg–Kohn energy functional and the question of \( N \)-representability will be mentioned. This chapter closes the sequence of theoretical introduction, and the main body of our work starts in the next one. The first of these chapters is about the MRA expansion of the quantities introduced in the first part of the dissertation, from density matrices to energy terms, and the expansion coefficients’ and basis functions’ structure is also stud-
ied. In Chapter 6 I will describe a method for reproducing a previously given density by multiresolution analysis, and give the possible expansion coefficients of the corresponding one-electron density matrices for different types of systems. Some conclusions about the kinetic energy functionals are also drawn. Next, the adaptive refinement of resolution follows, which is an algorithmic tool for introducing more detailed descriptions of the electron structure in only those spatial regions, where it is required. In the last chapter the electron-electron cusp condition is reproduced in a very natural manner using wavelet basis, and an interesting scaling property of the expansion coefficients is shown.

Except for some cases, the basic ideas are originated to my supervisor, the analytical calculations are mostly elaborated together, and the numerical realization was my project. If this is not the case, it is mentioned in the text.
Chapter 1

Multiresolution analysis

1.1 The history of wavelets

The first wavelet can be connected to Alfred Haar [36], it appeared in his article about the Theory of Orthogonal Function Systems in 1910, although it was not named as wavelet. The name itself came much later from the French word for little waves – the pioneers of the field were French. Many forerunners of wavelet analysis existed in separated disciplines, like the Gabor transform [37], the short time and windowed Fourier transform, the Calderón formula [38], the Littlewood–Paley theory [39], the coherent state theory of Klauder and Skägerstam [40] and Morelet’s fixed shape wavelets.

Morelet worked as geophysicist for an oil company and developed a signal processing method, which was more sensitive in the low frequency region, than the commonly used Fourier analysis. (Of course, as a geophysicist, he used the algorithm for seismic signals.) Since no mathematics books contained his method, he published his experience in collaboration with Grossmann [41]. Grossmann had studied coherent states, and found out the theoretical similarities between the two topics. Soon, Meyer shed light on the connection between Mallat’s and Grossmann’s method and the harmonic analysis [42], [43]. The harmonic analysis was a branch of Fourier analysis, and a common belief held, that the wavelet systems did not constitute a basis, but a frame system (which means, that although any function of the space can be expanded by frames, the expansion is not unambiguous, the frames are not orthogonal to each other). By building an orthonormal wavelet system Meyer has disproved this common belief, arousing many people’s interest in the field.

Similarly to the Fourier analysis–Fourier series duality, there exists continuous and discrete wavelet transform, as well. The basic theory of the discrete transform was developed by S. Mallat [44], who had found wavelets extremely useful in his work of image processing, because they could treat the more detailed parts locally with a finer resolution, and the rougher parts
on larger grid, in contrast with the Fourier series based methods, which were only able to process the whole picture either in a rougher or in a finer resolution level, causing either too large deterioration of the image, or too small data compression rate. Mallat’s theory is called multiresolution analysis (MRA), and its motivation was the Laplacian pyramid transform. His definitions will be followed in this chapter.

Another great step in the wavelets’ history was Daubechies’s work ([45], [46], [47], summarized in [33]), where she presented an easily understandable method for generating compactly supported, orthonormal wavelet families with different regularity properties. (A function is compactly supported, if its value is exactly zero outside of an interval, outside of its support.)

Today wavelets have a mathematically satisfactory background, and they are used in various fields of science and engineering. The first application was signal processing, and one of the leading application of MRA is the wavelet analysis of different types of data, from seismic signals to molecular physics, to noise reduction. Mathematicians developed differential equation solving, wavelet based methods (summarized e.g. in [48]–[50]). The driving force is the compression of pictures, better wavelets and easier transformation algorithms are always welcome. The first MRA applying image processing program was the FBI’s fingerprint database, now many other picture compressing algorithms are available, as a recent example, I mention JPEG2000.

Wavelets are also used in electron structure calculations. Leherte analyzed wave functions of different molecules arising from other calculations using MRA [51]. Density functional calculations can also be executed using wavelets. Goedecker and Ivanov [52] solved the Poisson equation, Cho et al. employed wavelets in solving the Schrödinger equation for Hydrogen-like atoms [53]. Later, all electron calculations were also performed within the limits of the local density approximation (LDA, see e.g. in [20]) using pseudopotentials and supercells [31], Car–Parinello algorithm [54] and in [55] a new approach for magnetic ordering was presented. Arias and his coworkers developed Kohn–Sham equations [15] based MRA method [56], and also tested for various systems, e.g. [57] and [58].

1.2 The definition of scaling functions and MRA

I am going to start with the following abstract mathematical definition. Multiresolution analysis of the square integrable functions’ Hilbert space $L^2(\mathbb{R})$ is a sequence of its closed subspaces $\{V_m, m \in \mathbb{Z}\}$ that meets the following properties

- $\forall m \in \mathbb{Z}$, $V_m \subset V_{m+1}$, i.e., the subspaces are embedded in each other, $V_m$ contains all the subspaces $V_n$ with $n < m$.
- $\exists a > 1$ $v(r) \in V_m \iff v(ar) \in V_{m+1}$, i.e., dilating the functions of
1.2. The definition of scaling functions and MRA

any subspace $V_m$ by a constant $a$, which is the same for all $m$, leads into the next, finer subspace.

- $\exists b > 0 \ v(r) \in V_0 \iff v(r - b) \in V_0$, i.e., translation of a function of the zero level subspace by a constant $b$ does not lead out of the subspace. This statement together with the previous one gives similar conditions for any subspace $V_m$, the difference is in the value of the translation constant, which is $2^{-mb}$.

- $\bigcap_{m=\infty}^{\infty} V_m = \{0\}$ and $\bigcup_{m=-\infty}^{\infty} V_m$ is dense in $L^2(\mathbb{R})$.

- there exists a scaling function $s_0 \in V_0$ with a non-vanishing integral, such that the collection $\{s_0(r - b\ell) | \ell \in \mathbb{Z}\}$ is an orthonormal basis of $V_0$. It is not necessary to demand orthogonality, but practical considerations deem it advisable.

The orthonormal basis of subspace $V_m$ is the set of functions: $\{s_m\ell(r) | \ell \in \mathbb{Z}\}$, where $s_m\ell(r) = a^{m/2} s_0(a^mr - b\ell)$. The values $a = 2$ and $b = 1$ are commonly used, I will follow this convention, too.

In order to give a visual point of view of the reason, why such a structure can be useful, let me introduce an analogy with a commonly known situation. Let us imagine, we want to measure distance between two objects. We have different units, even in the metrical system, there are kilometers, meters, millimeters or microns. For a distance between two cities, kilometer is the sufficient unit, although it could have been expressed in meters or even nanometers. On the other hand, for the distance between two cells in the body of a cat, we would get zero in kilometers or meters, much finer units are necessary. Similarly the Hilbert space of square integrable functions is separated into different resolution levels, some functions can already be expanded at low resolution levels, while some with many tiny details need extremely high resolution expansion. The most important property of the MRA is that these subspaces are embedded in each other, i.e., returning to our analogous example, if a distance can be given in whole meters exactly, it will be able to be expressed in whole millimeters, microns and nanometers, as well. It is possible, because meter can be given in whole units of millimeters, microns, and so on. Thus it is natural to demand that the basis functions of a rougher resolution level $m$ should be expandable by the scaling functions of the finer levels $n > m$. For $n = m + 1$, this formula is called refinement equation and looks like as follows

$$s_m\ell(r) = \sum_{k=0}^{N_s} p_k s_{m+1,k+2\ell}(r) \quad (1.1)$$

with $\sum_{k=1}^{N_s} p_k = 2$. In principle, the summation in the refinement equation could be infinite, but it is favorable, and possible to choose only a finite
number of non-zero expansion coefficients \( p_k \). In this case it is proved [34], that the mother scaling function \( s_0 \) has finite support, \( s_0 \) is zero outside of the interval \([0, N_s]\). Knowing the value of \( s_0 \) at the integer points between 0 and \( N_s \), the iterative application of (1.1) offers a possibility for calculating the value of \( s_0(r) \) at any diadic points \( r = 2^{-m}n \) for any integers \( m \) and \( n \). Since \( s_0 \) is continuous [33], the refinement equation completely determines the scaling function, provided that the values of \( p_\ell \), \( \ell = 0, \ldots, N_s \) are known. Finding an appropriate set of \( \{p_\ell\} \) is not an easy task, but many possible choices are known [33, 34]. Just to mention a few examples, the Haar scaling function’s non-zero expansion coefficients are \( p_0 = 1 \) and \( p_1 = 1 \) resulting in a scaling function plotted in the left hand side of Fig. 1.1. We are also going to apply Daubechies-4 basis set, which is one of the simplest, which has a support length larger than 1, with the generating coefficients \( p_0 = (1 + \sqrt{3})/4, p_1 = (3 + \sqrt{3})/4, p_2 = (3 - \sqrt{3})/4 \) and \( p_3 = (1 - \sqrt{3})/4 \), and which is also shown in Fig. 1.1.

Figure 1.1: Mother scaling functions of the basis sets of Haar and Daubechies-4.

Neither of these two functions are differentiable everywhere, but the Daubechies-4 is continuous and differentiable once (in Lebesgue measure) almost everywhere. Enlargement of the support leads to even more regular functions, e.g. the Daubechies-6 is differentiable once everywhere.

A function \( f \in L^2(\mathbb{R}) \) can be projected onto subspaces of any resolution level \( m \), thus an \( m \)th level approximation of the function arises in the following way

\[
f^{[m]}(r) = \sum_\ell c_{m\ell} s_{m\ell}(r), \tag{1.2}
\]

with \( c_{m\ell} = \langle \tilde{s}_{m\ell} | f \rangle \). The dual \( \tilde{s}_{m\ell}(r) \) of the scaling function can be calculated, and have similar scaling properties to the original \( s_{m\ell} \). In case of self-dual systems, like the Haar and all the Daubechies sets, the expansion coefficients in Eq. (1.2) will simply turn into \( c_{m\ell} = \langle s_{m\ell} | f \rangle \).

The extension into 3 dimensions is straightforward, \( V_m(\mathbb{R}) \otimes V_m(\mathbb{R}) \otimes V_m(\mathbb{R}) = V_m(\mathbb{R}^3) \), and the three dimensional scaling functions can be chosen as the direct products of functions \( s_{mk} \) [59]–[61]. There also exist 3D scaling
functions, which can not be generated from 1D scaling functions.

### 1.3 Wavelets

The set of subspaces \( \{ V_m | m = 0, 1, \ldots \} \) cover some parts of the Hilbert space \( L^2(\mathbb{R}) \) multiple times. Let the detail space \( W_m \) be the orthogonal complement of \( V_m \) in the finer subspace \( V_{m+1} \)

\[
V_{m+1} = V_m \oplus W_m. \tag{1.3}
\]

In \( W_m \) a basis set can be defined as \( \{ w_{m\ell}(r) | \ell \in \mathbb{Z} \} \) with the basis functions \( w_{m\ell}(r) = 2^{m/2} w_0(2^{-m} r - \ell) \) generated from one function \( w_0 \) by dilations and contraction, similarly to the scaling functions. Function \( w_0 \) is called mother wavelet, and the elements of the basis set \( \{ w_{m\ell}(r) | \ell \in \mathbb{Z}, m = 0, 1, \ldots \} \) are the wavelets. Wavelets are also compactly supported, if the scaling functions are of that kind, and can also be generated from the coefficients \( p_k \) and from the scaling functions using the following equation

\[
w_{m,\ell}(r) = \sum_{k=1-N_s}^{1} q_k s_{m+1} 2^{\ell-k}(r) \tag{1.4}\]

with \( q_k = (-1)^k p_{-k+1}^* \). The sign * means complex conjugation. There exist a transformation that gives the finer resolution scaling functions from the lower level basis functions and can be summarized in the formula

\[
s_{m+1} 2L+b(r) = 2^{-1/2} \sum_{K=0}^{(N_s-1)/2} p_{2K+b}^* s_{m} L-K(r) \]

\[+ 2^{-1/2} \sum_{K=-(N_s-1)/2}^{0} q_{2K+b}^* w_{m} L-K(r), \tag{1.5}\]

for \( b = 0, 1 \). It is clear that the even indexed fine scaling functions arise from the even indexed rough wavelets and scaling functions in their support, and similar statement holds for the odd indices.

### 1.4 Refinement of the approximation: the pyramid algorithm

This structure of subspaces makes possible to use the already existing \( m_0 \)th level expansion, and refine it, with the \( m_0 \)th level wavelets thus getting \((m_0 + 1)\)th level approximation, which can be again approved to level \( m_0 + 2 \) by using the wavelets of resolution level \( m_0 + 1 \), etc. The whole Hilbert space
of the square integrable functions can be segmented as
\[ L^2(\mathbb{R}) = \bigoplus_{m=m_0}^{\infty} W_m \oplus V_{m_0} \] (1.6)

with any starting resolution level \( m_0 \). If an \( m_1 \)th level expansion is sufficient (of course, \( m_1 > m_0 \)),
\[ V_{m_1} = \bigoplus_{m=m_0}^{m_1-1} W_m \oplus V_{m_0} \] (1.7)

holds, which means, that the \( m_1 \)th level approximation of a function \( f \in L^2(\mathbb{R}) \) can be given either in the basis \( \{s_{m_1k}|k \in \mathbb{Z}\} \) or in \( \{s_{mk}, w_{mk}|k \in \mathbb{Z}, m=m_0, m_0+1, \ldots, m_1-1\} \) as
\[ f^{[m_1]}(r) = \sum_k c_{m_1k} s_{m_1k}(r) \] (1.8)
\[ f^{[m_1]}(r) = \sum_k c_{mk} s_{mk}(r) + \sum_{m=m_0}^{m_1-1} \sum_k d_{mk} w_{mk}(r). \] (1.9)

Let us suppose, that the function \( f \) is compactly supported in the interval \( J \) of length \( 2^{-m_1}J \), with a given integer \( J \). The number of coefficients \( \{c_{m_1k}\} \) in expansion (1.8) equals to the number of coefficients \( \{c_{mk}, d_{mk}\} \) in (1.9), in both cases it is \( J \), independently of the starting level \( m_0 \). However, it is not necessary to keep all the expansion coefficients \( d_{mk} \), if in a region lower resolution level is sufficient. If either of the two sets is known, the other can be calculated using Eqs. (1.1), (1.4) and (1.5) in the following way. Let \( c_m \) and \( d_m \) denote the vector built from the \( m \)th level scaling function and wavelet coefficients of the function in the interval \( J \), respectively (\( m_0 \leq m \leq m_1 \)). The decomposition, i.e., calculation of the rougher coefficients from the finer ones can be summarized in the two matrix equations
\[ c_{m-1} = Lc_m \quad \text{and} \quad d_{m-1} = Hc_m, \] (1.10)

where the non-square matrices \( L \) and \( H \) are built from the coefficients in Eqs. (1.1) and (1.4), respectively, as \( L_{i,j} = p_{j-2i+1} \) and \( H_{i,j} = q_{j-2i+1} = (-1)^{j+1}p_{2i-j}^* \). The size of these matrices is \( 2^{m_1-m}J \times 2^{m_1-m+1}J \). The reconstruction, i.e., the transformation from the rough \( c_{m-1} \) and \( d_{m-1} \) to the fine scaling function coefficients goes as follows
\[ c_m = L^*c_{m-1} + H^*d_{m-1}. \] (1.11)

The scheme given by Eqs. (1.10) and (1.11) is usually mentioned as ladder algorithm, since the shape of its chart flow diagram reminds a ladder
\[ \begin{align*}
&c_{m_1} \xrightarrow{L} c_{m_1-1} \xrightarrow{L} c_{m_1-2} \xrightarrow{L} \ldots \xrightarrow{L} c_{m_0+1} \xrightarrow{L} c_{m_0} \\
&\downarrow H \quad \downarrow H \quad \downarrow H \quad \ldots \quad \downarrow H \\
&d_{m_1-1} \xrightarrow{L} d_{m_1-2} \xrightarrow{L} d_{m_1-1} \xrightarrow{L} d_{m_0}
\end{align*} \] (1.12)

or pyramid algorithm because of its origin, the family of pyramid algorithms.
1.5 Partition of unity and vanishing moments

In this section some properties of the MRA basis set are mentioned, which help to reproduce functions more easily than other types of basis sets. First, any constant function is always expandable at any resolution levels, since

$$\sum_\ell s_{m\ell}(r) = 1, \quad \forall r \in \mathbb{R}, \quad (1.13)$$

is valid at any $m$. This equation is called the partition of unity, and this causes the slowly varying functions to be extremely well reproducible, already at moderate resolution levels. Second, if the first $A$ moments of the scaling function vanish, i.e., if

$$\int_{-\infty}^{\infty} r^a s_0(r) = 0, \quad \text{for } a = 1, 2, \ldots, A \quad (1.14)$$

holds, any polynomial of order not greater than $A$ is exactly expandable at any resolution level $m$. The Haar scaling function has no vanishing moments, the Daubechies-4 scaling function has one, but there exist many, a bit more complex systems with higher vanishing moments. The coiflets [33], [62] are built in order to achieve the maximum number vanishing moments for a given support length $N_s$.

The reason, why MRA is so successful in so many fields of science and engineering, is not just that they are very flexible and adaptable to the signal shapes, but the capability of processing or storing the data locally at different resolution levels, as the complexity of the function in the given region of space demands.
Chapter 2

Density matrices and density operators

2.1 N-electron density matrices

Since the Hohenberg–Kohn theorem was published, a great interest rose in the field of electron density and density matrices, hoping that all the essential properties of the system can be derived from these quantities, ignoring the $N$-particle wave function.

Let $\Psi(x_1, \ldots, x_N)$ be the wave function of an $N$-electron system. The variables $x_i$ consist of space variables $r_i$ and spin variables $\sigma_i$. According to e.g. [63] and [64] the pure state, $N$-particle density matrix arises from the wave function as

$$\gamma_N(x_1, \ldots, x_N | x'_1, \ldots, x'_N) = \Psi(x_1, \ldots, x_N) \Psi^*(x'_1, \ldots, x'_N). \quad (2.1)$$

Function $\gamma_N$ of $2 \times 4N$ variables is the kernel function of the density operator $\Gamma_N = |\Psi\rangle \langle \Psi|$, i.e., the effect of the density operator on any wave functions $\phi$ can be expressed as

$$(\Gamma_N \phi)(x_1, \ldots, x_N) = \int \gamma_N(x_1, \ldots, x_N | x'_1, \ldots, x'_N) \phi(x'_1, \ldots, x'_N) dx'_1 \ldots dx'_N. \quad (2.2)$$

with the integral measure $dx'_i$ meaning integration for the space variables $r'_i$, and summation for the spin variables $\sigma'_i$. From definition (2.1) follows, that the density operator $\Gamma_N$ is a Hilbert–Schmidt operator [65], [66].

Clearly, $\gamma_N$ is hermitic as

$$\gamma_N(x_1, \ldots, x_N | x'_1, \ldots, x'_N) = \gamma_N^*(x'_1, \ldots, x'_N | x_1, \ldots, x_N), \quad (2.3)$$

and the Pauli principle is fulfilled by the symmetry properties

$$\gamma_N(x_1, x_2, \ldots, x_N | x'_1, x'_2, \ldots, x'_N) = -\gamma_N(x_2, x_1, \ldots, x_N | x'_1, x'_2, \ldots, x'_N) = \gamma_N(x_2, x_1, \ldots, x_N | x'_2, x'_1, \ldots, x'_N). \quad (2.4)$$

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2.2 Reduction of degrees of freedom

The $N$-electron density matrix contains redundant information about the system. Since a real, physical Hamiltonian operator consists of only one- and two-electron operators, two degrees of freedom is sufficient to describe the system, the other $N-2$ are superfluous. Consecutive application of partial trace operations

$$\gamma_p(x_1, \ldots, x_p | x'_1, \ldots, x'_p) = \frac{p+1}{N-p} \int \gamma_{p+1}(x_1, \ldots, x_{p+1}, x'_1, \ldots, x'_{p+1}) \, dx_{p+1},$$

(2.5)

can result in the reduction of degrees of freedom to two. Löwdin’s normalization condition $\int \gamma_p(x_1, \ldots, x_p | x_1, \ldots, x_p) \, dx_1 \cdots dx_p = \binom{N}{p}$ is used. This way of reduction of degrees of freedom is also called contraction. A $p$-electron density matrix is contracted from the original, $N$-electron one, if $p < N$ as [67]

$$\gamma_p(x_1, \ldots, x_p | x'_1, \ldots, x'_p) = \binom{N}{p} \int \gamma_N(x_1, \ldots, x_p, x_{p+1}, \ldots, x_N | x'_1, \ldots, x'_p, x_{p+1}, \ldots, x_N) \times dx_{p+1} \cdots dx_N.$$

(2.6)

The reduced density matrix $\gamma_p$ owns the following important properties. It is positive semidefinite and Hermitic, i.e.,

$$\gamma_p(x_1, \ldots, x_p | x'_1, \ldots, x'_p) = \gamma_p(x'_1, \ldots, x'_p | x_1, \ldots, x_p)^*.$$  

(2.7)

The Pauli principle manifests in symmetry properties similar to (2.4). A $p$-particle observable physical quantity $\hat{h}$ has the expectation value

$$\langle \hat{h} \rangle = \int \left[ \hat{h}(x_1, \ldots, x_p) \gamma_p(x_1, \ldots, x_p | x'_1, \ldots, x'_p) \right] x'_1=x_1 \, dx_1 \cdots dx_p$$

$$\vdots$$

$$x'_p=x_p$$

$$= \text{Tr} \left( \Gamma_p \hat{h} \right).$$

(2.8)

The operators representing real physical observables are usually one- or two-electron operators.

2.3 Spin tracing

In some cases, spin variables are not necessary, summation for the spins can be carried out, resulting in a spin-traced density matrix of order $p$

$$\gamma_p^\sigma(r_1, \ldots, r_p | r'_1, \ldots, r'_p) = \sum_{\sigma_1, \ldots, \sigma_p} \gamma_p(r_1, \sigma_1, \ldots, r_p, \sigma_p | r'_1, \sigma_1, \ldots, r'_p, \sigma_p).$$

(2.9)
2.3. Spin tracing

The symmetry properties of $\gamma_s^p$ can be originated from those of $\gamma_p$

$$\gamma_s^p(r_1, r_2, \ldots, r_p|r'_1, r'_2, \ldots, r'_p) = \gamma_p^s(r_2, r_1, \ldots, r_p|r'_2, r'_1, \ldots, r'_p)$$

$$= (\gamma_p^s(r'_1, r'_2, \ldots, r'_p|r_1, r_2, \ldots, r_p))^*.$$  \hspace{1cm} (2.10)

Usually $\gamma_s^p(r_1, r_2, \ldots, r_p|r'_1, r'_2, \ldots, r'_p) \neq -\gamma_p^s(r_2, r_1, \ldots, r_p|r'_2, r'_1, \ldots, r'_p)$ except for the cases, when all the electrons have the same spin, i.e., in ferromagnetic phases, where the total spin is $S = N/2$. 
Chapter 3

Kato’s cusp conditions

In 1957, Kato showed [32], that the wave functions of many electron molecules have cusps in the points, where one of the electrons is located at the position of one of the nuclei or of one of the other electrons. The equations, describing these point singularities are generalized and adapted to many requirements [68]–[72], resulting in formulas, which are on the one hand very helpful in molecular physics calculations, on the other hand sometimes very hardly reproducible. Especially, producing wave functions which meet the electron-electron cusp condition is a hard task. As a compromise explicit \((r_i - r_j)\) dependence can be introduced to the trial \(N\)-electron wave function. Slater determinants are usually multiplied by a Jastrow factor, an appropriately chosen function of \((r_i - r_j)\), where \(r_i\) and \(r_j\) denote the space coordinates of the \(i\)th and \(j\)th electrons. (A summary of the Jastrow factor method can be found in Ref. [73].)

In MRA basis, however, it is possible to develop a method for expanding this correlation cusp condition, as well.

3.1 Nuclear cusp condition of the electron density

Let \(\hat{H}\) be the \(N\)-electron Hamiltonian in the form

\[
\hat{H} = \sum_{i=1}^{N} \left( -\frac{1}{2} \Delta_i - \sum_{\alpha} Z_{\alpha} \frac{r_{i\alpha}}{r_{i\alpha}} \right) + \sum_{i<j} \frac{1}{r_{ij}},
\]

(3.1)

where \(r_{ij}\) is the distance between the \(i\)th and \(j\)th electron, \(Z_{\alpha}\) is the charge of the \(\alpha\)th nucleus, and \(r_{i\alpha}\) is its distance from the \(i\)th electron. The wave function of the Schrödinger equation \(\hat{H}\Psi = E\Psi\) with this Hamiltonian will be singular at the points \(r_{i\alpha} = 0\), and \(r_{ij} = 0\). Without losing the generality, we can choose the 1st electron to be in the focus of our interest. At the point \(r_{1\alpha} = 0\) the wave function \(\Psi\) can be averaged over the spherical...
CHAPTER 3. KATO’S CUSP CONDITIONS

angles $\theta_1$ and $\phi_1$ according to

$$\Psi(r_1, r_2, \ldots, r_N) = \int_0^{2\pi} \int_0^\pi \Psi(r_1, \theta_1, \phi_1, r_2, \ldots, r_N) d\theta_1 d\phi_1. \quad (3.2)$$

The slope of the resulting function $\bar{\Psi}$ is

$$\left( \frac{\partial \bar{\Psi}}{\partial r_1} \right)_{r_1=0} = -Z\alpha \Psi(0, r_2, \ldots, r_N). \quad (3.3)$$

This formula can also be deduced for the electron density as

$$\left( \frac{\partial \bar{\rho}(r_1)}{\partial r_1} \right)_{r_1=0} = -2Z\alpha \rho(0) \quad (3.4)$$

with $\bar{\rho}(r)$ being the spherical average of the density $\rho(r)$ arising similarly to $\bar{\Psi}$ in (3.2) by integrating over the spherical angles $\theta$ and $\phi$ belonging to the variable $r$.

3.2 Electron-electron cusp condition of the two-particle density matrix

Because of the antisymmetry of the wave function we can choose to study the coincidence of the electrons 1 and 2, instead of arbitrary indices $i$ and $j$, without losing the generality. Following Kato’s train of thought in the deduction of the electron-electron, or correlation cusp condition, the center $R = (r_1 + r_2)/2$, and the distance $u = r_1 - r_2$ of the two electrons can be introduced from the first and second electrons’ coordinates. The singularity occurs at point $u = 0$. After taking the spherical average of the wave function similarly to (3.2), according to the spherical angles of variable $u$, the singularity condition can be written as

$$\left( \frac{\partial \bar{\Psi}}{\partial u} \right)_{u=0} = \frac{1}{2} \Psi(0, 0, r_3, \ldots, r_N), \quad (3.5)$$

where $u$ is the radial part of $u$ and $R = 0$.

Bingel showed in [68] that these conditions are equivalent to

$$\Psi(r_1, r_2, \ldots, r_N) = \Psi(R, R, r_3, \ldots, r_N)(1 + \frac{1}{2}u) + u \cdot c_{12}(R, r_3, \ldots, r_N) + \ldots, \quad (3.6)$$

where vector $c$ is not determined by the Coulomb interaction.

In his article in 1966 [69] Bingel adapted these conditions for the two-particle density matrices $\gamma_2^s$, writing Eq. (3.6) for both $\Psi$ and $\Psi^*$, formulating
3.2. Electron-electron cusp condition of the two-particle density matrix

Nth order density matrix from them according to (2.1), then contracting $\gamma_N$ using (2.6) with $p = 2$. The new center and difference coordinates

\[
\begin{align*}
R &= \frac{r_1 + r_2}{2}, & R' &= \frac{r'_1 + r'_2}{2}, \\
u &= r_1 - r_2, & u' &= r'_1 - r'_2
\end{align*}
\]

(3.7)

were also introduced, thus after spin tracing (2.9) the correlation cusp condition became

\[
\gamma^2_2(r_1, r_2|r'_1, r'_2) = \gamma^2_2(R, R|R', R') \left(1 + \frac{1}{2}u + \frac{1}{2}u'\right) + u \cdot d^*(R, R') + u' \cdot d(R', R) + \ldots,
\]

(3.8)

with $u = |u|$ and $u' = |u'|$ being sufficiently small, and $d$ is not determined by the Coulomb interaction. Vector $d$ can be connected to the quantity $c$ in Eq. (3.6) in the following way

\[
d(R', R) = \int c(R, r_3, \ldots, r_N)\Psi^*(R, r_3, \ldots, r_N)dr_3\ldots dr_N.
\]

(3.9)

The spin traced density matrix for spinless particles or ferromagnetic systems ($S = N/2$) shows the antisymmetry property $\gamma^2_2(r_1, r_2|r'_1, r'_2) = -\gamma^2_2(r_2, r_1|r'_1, r'_2)$, resulting in $\gamma^2_2(R, R|R', R') = 0$, thus the cusp condition (3.8) is trivial. The Bingel formula is meaningful only for systems with $S < N/2$. In condition (3.8), the vector $d$ is independent of the distance of the electrons $u$ and $u'$, thus averaging by the spherical angles of these coordinates by

\[
\overline{\gamma}(R, u) = \frac{1}{4\pi} \int \gamma^2_2 \left(R + \frac{u}{2}, R - \frac{u}{2} \right) \sin \theta_u d\theta_u d\phi_u,
\]

(3.10)

would eliminate it. Here the diagonal element with $R = R'$ and $u = u'$ was taken, and the notation $\theta_u, \phi_u$ covers the spherical angles of $u$, while $u = |u|$. This formula being substituted into (3.8) results in (in linear approximation)

\[
\overline{\gamma}(R, u) \approx \gamma^2_2(R, R|R, R) \left(1 + u\right).
\]

(3.11)

This condition is local in the sense, that it has to be valid at every point $R$. In many electron calculations (like e.g. [74, 75]) the global satisfaction of the correlation cusp condition is checked to the spatial average of (3.11). Note, that using $\gamma^2_2(R, R|R, R) = \overline{\gamma}(R, 0)$, the condition (3.11) can be translated to the well known formula

\[
\frac{\partial}{\partial u} \log \overline{\gamma}(R, u) \bigg|_{u=0} = 1.
\]

(3.12)

However, in this work the more general (3.8) and (3.11) conditions are used.
Chapter 4

Energy density functionals

4.1 Hohenberg–Kohn theorems

This summary is given following the work [16] and [20]. According to the Hohenberg–Kohn theorem [14], the ground state of a system with an external multiplicative potential $v$ can be unambiguously described by the ground state electron density, if the density is $v$-representable. (The problem of $v$-representability will be discussed in the next section.) This would allow to work with the density of 3 variables instead of the $4N$-variables wave function and write the Hamiltonian operator as a functional of the density $\rho$. Let us suppose, that the system consists of some atoms with spatially fixed nuclei and $N$ electrons. This approach is the Born–Oppenheimer approximation. The Coulomb potential of the nuclei (together with the external electric fields) gives the external potential $v(r)$. The Hamiltonian of an $N$-electron system in Born–Oppenheimer approximation can be separated into three parts, the kinetic energy of the electrons ($\hat{T}$), the electron-electron interaction ($\hat{W}$) and the external potential energy ($\hat{V}$). $\hat{W}$ is the only two-particle operator, the others consist of one-electron terms. For all the $N$-electron systems $\hat{K}$ and $\hat{W}$ are the same (the only difference is the position and size of the atoms and the external fields), thus they are usually treated together as $\hat{F}$. The Hohenberg–Kohn functional is the ground state expectation value of the kinetic and electron-electron interaction energy, as a functional of the density $F_{HK}[\rho]$.

The first Hohenberg–Kohn theorem states, that the electron density $\rho(r)$ determines $v$ up to an additive constant. The indirect proof for non-degenerate ground states is quite scenic. Let us suppose, that multiplicative potentials $v$ and $v'$ exist, they differ in more than an additive constant, and both of them leads to the same electron density $\rho$. If the Hamiltonians, which differ only in the external potential terms, are $\hat{H}$ and $\hat{H}'$, the ground state wave functions belonging to them are different, $\Psi \neq \Psi'$. This can be proved in the following way. Let us take the Schrödinger equation for both
\(H\) and \(H'\)

\[
\hat{H}|\Psi\rangle = E_0|\Psi\rangle \\
\hat{H}'|\Psi'\rangle = E'_0|\Psi'\rangle
\]

with the ground state energy of \(\hat{H}\) being \(E_0\), and of \(\hat{H}'\) being \(E'_0\). If the ground state wave functions were equal, \(|\Psi\rangle\), the two equations could be subtracted from each other, resulting in

\[
(v - v')|\Psi\rangle = (E_0 - E'_0)|\Psi\rangle.
\]

(4.1)

Since the potentials are multiplicative, formula (4.1) means, that the potentials differ in a constant, which is in contradiction with the primary assumption. Returning to the original proof, the variational principle for the Hamiltonian \(\hat{H}\), the wave functions \(|\Psi\rangle\) and \(|\Psi'\rangle\) and the ground state energy \(E_0\) says

\[
E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle
\]

\[
= E'_0 + \int (v(r) - v'(r)) \varrho(r)dr.
\]

(4.2)

However, if \(\hat{H}'\) and \(E'_0\) are studied, we get a similar statement

\[
E'_0 < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle
\]

\[
= E_0 + \int (v'(r) - v(r)) \varrho(r)dr.
\]

(4.3)

Adding the two equations (4.2) and (4.3) leads to the contradiction \(E_0 + E'_0 < E_0 + E'_0\), thus no such potentials exist, which differ not only in an additive constant and lead to the same density.

The second Hohenberg-Kohn theorem states, that for any non-negative, \(v\)-representable function \(\tilde{\varrho}(r)\), with \(\int \tilde{\varrho}(r)dr = N\) holding, the ground state energy given by \(\tilde{\varrho}\) with the Hamiltonian of the electron system cannot be less then the real ground state energy. This simply follows from the variational principle, by taking the expectation value of the Hamiltonian \(\hat{\tilde{H}}\) of the system with the wave function \(\tilde{\Psi}\), the ground state wave function of the Hamiltonian \(\hat{\tilde{\varrho}}\), which would arise according to the first theorem from \(\tilde{\varrho}\), if \(\tilde{\varrho}\) would be a density. In formulas the proof looks like

\[
\langle \tilde{\Psi} | \hat{\tilde{H}} | \tilde{\Psi} \rangle = F_{HK}[\tilde{\varrho}] + \int v(r)\tilde{\varrho}(r)dr \geq E_0.
\]

(4.4)

The variational principle, using this formalism and the requirement, that the electron number should be a constant \(N\) is

\[
\delta \left( F_{HK}[\varrho] + \int v(r)\varrho(r)dr - \mu \left( \int \varrho(r)dr - N \right) \right) = 0,
\]

with the Lagrangian multiplicator \(\mu\) being the chemical potential.
4.2 The \( v \)-representability of the electron density and Lieb’s functional

Not all the non-negative functions with integral of \( N \) can be generated from wave functions which are eigenfunctions of an \( N \)-electron Hamiltonian with external potential \( v \). The Hohenberg–Kohn theorems are only valid for \( v \)-representable densities, i.e., for densities arising from ground state wave functions of an \( N \)-particle Hamiltonian with any possible external potential \( v \). The Hohenberg–Kohn functional is then

\[
F_{HK}[\rho] = \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle
\]

with \( \Psi \) being that ground state electron wave function, which belongs to the \( v \)-representable density \( \rho \). From this, it follows that the variation in Eq. (4.5) is to be taken in the set of \( v \)-representable functions, which set is unknown, increasing the practical difficulties of finding the density and the ground state energy.

Levy [76], [77] and Lieb [78], [79] have proved, that among all the possible wave functions \( \Psi_{\rho_0} \) which result in the same ground state density \( \rho_0 \) the real ground state wave function \( \Psi_0 \) minimizes the expectation value \( \langle \Psi_{\rho_0} | \hat{T} + \hat{W} | \Psi_{\rho_0} \rangle \), while the external potential term is the same for all these wave function. Based on this fact, they have generalized the Hohenberg–Kohn functional as

\[
F_{LL}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle,
\]

where the notation \( \Psi \rightarrow \rho \) means, that the minimum has to be searched in the set of wave functions resulting in the given density \( \rho \). Of course, \( \rho \) has to be a density of a possible \( N \)-electron system, which brings up the problem of its \( N \)-representability. Fortunately, all positive semidefinite (\( \rho(r) \geq 0 \)) functions \( \rho \) with \( \int \rho(r)dr = N \) holding are \( N \)-representable. Searching among such densities, the ground state energy can be expressed as

\[
E_0 = \min_{\rho} \left( F_{LL}[\rho] + \int v(r)\rho(r)dr \right).
\]

Further extension of the Hohenberg–Kohn energy functional \( F_{HK}[\rho] \) is Lieb’s functional [79]–[81]

\[
F_{L}[\rho] = \inf_{\Gamma \rightarrow \rho} \text{Tr} \left\{ \Gamma(\hat{T} + \hat{W}) \right\}.
\]

Here, \( \Gamma \) is the \( N \)-electron density operator, \( \hat{T} \) and \( \hat{W} \) are the kinetic and electron-electron interaction energy operators of the system, respectively. Symbol \( \Gamma \rightarrow \rho \) means that the infimum has to be searched over all the density operators which produce the fixed density \( \rho \). The ground state energy of an electron structure with external potential \( v(r) \) is expressed as
\( E_0 = \min_\rho (F_L[\rho] + \int v(r)\rho(r)dr) \). Of course, methods for finding all the density operators resulting in the same density are still not found.

For one particle density operators the problem of \( N \)-representability is solved, it belongs to a real fermionic physical system, if and only if its eigenvalues are between 0 and 1 (or for spin-traced density operators 0 and 2). This necessary and sufficient condition is called the generalized Pauli principle \([82]\). For two particle density operators necessary conditions are known for \( N \)-representability, however, sufficient condition does not exist yet.

### 4.3 Energy terms

Using the spin-traced one- and two-electron density matrices, the kinetic energy, electron-electron interaction, and external potential energy expectation values can be expressed as

\[
\langle T \rangle = \frac{1}{2} \int \left( \frac{d}{dr} \frac{d}{dr'} \gamma_{12}^i(r|r') \right) dr \quad \text{(4.10)}
\]

\[
\langle W \rangle = \int \frac{\gamma_{12}^i(r_1,r_2|1_1,1_2)}{|r_1 - r_2|} dr_1 dr_2 \quad \text{(4.11)}
\]

\[
\langle V \rangle = \int g(r)v(r)dr, \quad \text{(4.12)}
\]

where \( v(r) \), the external potential is usually a sum of terms in the form \( Z_\alpha |r - R_\alpha|^{-1} \), where \( R_\alpha \) indicates the site of the \( \alpha \)th nucleus with charge \( Z_\alpha \). This means, that in Lieb’s density functional formula (4.9), it is enough to search the infimum in the set of \( N \)-representable two-electron density matrices resulting in the given density \( \rho \).
Chapter 5

The MRA expansion of the density matrices

After giving the short theoretical summary in the previous chapters, I turn now to presentation of our contributions to the field of MRA expansions applied to the \( N \)-electron structure calculations. The results in this chapter are mainly achieved by consultations and thinking together with my supervisor, except for the second section, which is purely his work, and some theoretically easy but algebraically complicated calculations (like the reduction of degrees of freedom), which were elaborated and tested for simple cases by me.

5.1 Expansion of the density matrices

For spin variables we have extended the definition of scaling functions and wavelets by introducing scaling function and wavelet spinors for one-electron basis set as

\[
s_m(x) = s_{m\ell s}(r, \sigma) = s_{m\ell}(r) \delta_{s\sigma},
\]

and

\[
w_m(x) = w_{m\ell s}(r, \sigma) = w_{m\ell}(r) \delta_{s\sigma}.
\]

In order to simplify the notations, I will remain at the basis set consists of purely scaling functions. The following considerations are also valid for objects built purely from wavelets or mixed from scaling functions and wavelets.

In order to reflect the antisymmetry properties of the \( N \)-electron wave functions, we have built Slater determinants from spinors (5.1)

\[
\chi_{\mu}(x_1, \ldots, x_N) = (N!)^{-1/2} \begin{vmatrix} s_{m_1}(x_1) & \ldots & s_{m_1}(x_N) \\ \vdots & \ddots & \vdots \\ s_{m_N}(x_1) & \ldots & s_{m_N}(x_N) \end{vmatrix},
\]
where multiindex $\mu$ denotes the set of indices $\mu = (m_1, \ldots, m_N)$. A general $N$-particle wave function $\Psi$ can be written as

$$\Psi(x_1, \ldots, x_N) = \sum_\mu c_\mu \chi_\mu(x_1, \ldots, x_N)$$

(5.4)

with complex coefficients $c_\mu = \alpha_\mu + i\beta_\mu$, where $\alpha_\mu$ and $\beta_\mu$ are real.

Substituting $\Psi$ by its wavelet decomposition (5.4) into the expression of the pure state, $N$-particle density matrix (2.1), after straightforward algebraic manipulations we have arrived at

$$\gamma_N(x_1, \ldots, x_N|x'_1, \ldots, x'_N) = \sum_{\mu \in O_N} p_\mu P_\mu(x_1, \ldots, x_N|x'_1, \ldots, x'_N)$$

$$+ \sum_{\mu \neq \nu \in O_N} a_{\mu\nu} A_{\mu\nu}(x_1, \ldots, x_N|x'_1, \ldots, x'_N)$$

$$+ \sum_{\mu \neq \nu \in O_N} b_{\mu\nu} B_{\mu\nu}(x_1, \ldots, x_N|x'_1, \ldots, x'_N).$$

(5.5)

The summation goes only for those vector indices $\mu = \{m_1, \ell_1, s_1, \ldots, m_N, \ell_N, s_N\}$ and $\nu = \{n_1, k_1, t_1, \ldots, n_N, k_N, t_N\}$, whose elements are ordered. The ordering can be e.g. increasing $m_i$ or $n_i$, if they are equal, increasing $\ell_i$ or $k_i$, and last increasing spin index $s_i$ or $t_i$. If the ordered index set $O_N$ is not introduced, and the summation in (5.5) is for all the indices, one term would be counted many times, and a prefactor $N^{-2}$ should be taken. The basis functions of $\gamma_N$ in (5.5) are the following combinations of the Slater determinants (5.3)

$$P_\mu(x_1, \ldots, x_N|x'_1, \ldots, x'_N) = \chi_\mu(x_1, \ldots, x_N) \chi^*_\mu(x'_1, \ldots, x'_N)$$

(5.6)

and for $\mu \neq \nu$

$$A_{\mu\nu}(x_1, \ldots, x_N|x'_1, \ldots, x'_N) = \chi_\mu(x_1, \ldots, x_N) \chi^*_\nu(x'_1, \ldots, x'_N)$$

$$+ \chi_\nu(x_1, \ldots, x_N) \chi^*_\mu(x'_1, \ldots, x'_N)$$

(5.7)

and

$$B_{\mu\nu}(x_1, \ldots, x_N|x'_1, \ldots, x'_N) = i[\chi_\mu(x_1, \ldots, x_N) \chi^*_\nu(x'_1, \ldots, x'_N)$$

$$- \chi_\nu(x_1, \ldots, x_N) \chi^*_\mu(x'_1, \ldots, x'_N)]$$

(5.8)

Note, that the expanding functions $P_\mu$ can be interpreted as the diagonal $2A_{\mu\mu}$. Similar diagonal functions $B_{\mu\mu}$ would be zero. As it easily follows from definitions (5.6)–(5.8) these basis functions meet the symmetry properties (2.3) and (2.4) of $\gamma_N$, which could be most easily summarized by introducing the operators corresponding to the kernel functions (5.6)–(5.8) (similarly to (2.2) in the relation of $\gamma_N$ to $\Gamma_N$), and telling their symmetry and normalization properties. The effect of an operator $P_\mu$ on a wave function $\phi$
is $(\hat{P}_\mu \phi)(x_1, \ldots, x_N) = \int P_\mu(x_1, \ldots, x_N|x'_1, \ldots, x'_N) \phi(x'_1, \ldots, x'_N) dx'_1 \ldots dx'_N$, the effect of the other two operators $\hat{A}_{\mu \nu}$ and $\hat{B}_{\mu \nu}$ are analogue to this. The index symmetries of the operators are $\hat{P}_\mu = \hat{P}_\mu^\dagger$, $\hat{A}_{\mu \nu} = \hat{A}_{\nu \mu}^\dagger$, $\hat{B}_{\mu \nu} = \hat{B}_{\nu \mu}^\dagger$, moreover $\hat{A}_{\mu \nu} = \hat{A}_{\nu \mu}^\dagger$, $\hat{B}_{\mu \nu} = -\hat{B}_{\nu \mu}^\dagger$. It is easy to see that $\text{Tr} \hat{P}_\mu = N$, $\text{Tr} \hat{A}_{\mu \nu} = 0$ and $\text{Tr} \hat{B}_{\mu \nu} = 0$, resulting in $\text{Tr} \hat{\Gamma}_N = \sum_\mu p_\mu = N$.

The expansion coefficients in (5.5) are connected to the wave function coefficients by

$$p_\mu = \alpha_\mu^2 + \beta_\mu^2, \quad a_{\mu \nu} = \frac{\alpha_\mu \alpha_\nu + \beta_\mu \beta_\nu}{2}, \quad b_{\mu \nu} = \frac{\beta_\mu \alpha_\nu - \beta_\nu \alpha_\mu}{2}. \quad (5.9)$$

As expressions (5.9) show $p_\mu \geq 0$, $a_{\mu \nu} = a_{\nu \mu}$, $b_{\mu \nu} = -b_{\nu \mu}$ and all of these quantities are real numbers.

### 5.2 Contributions of extremely fine and rough details

From the theory of compact operators (see e.g. [65]) is known that for an orthonormal sequence $\lim_{j \to \infty} \Gamma_N \chi_{\tau_j} = 0$.

In order to estimate the contributions of fine (or rough) wavelets to the density matrix $\gamma_N$, a wavelet index set $\tau = (t_1, \ldots, t_N)$ was chosen, and the indices $t_2, \ldots, t_N$ were kept constant, but at the same time the dilation index $m$ of $t_1 = (j, \ell)$ tended to $\infty$ (refinement) or to $-\infty$ (roughening). For any $j$ the corresponding index set $\tau_j$ defines an $N$-electron basis function $\chi_{\tau_j}$. The set of basis functions $\{\chi_{\tau_j}\}$ is an infinite orthonormal sequence as $j \to \infty$.

For an arbitrary index set $\tau$ (5.5) and (2.2) resulted in

$$\Gamma_N \chi_\tau = \sum_\mu p_\mu \chi_\mu \langle \chi_\mu | \chi_\tau \rangle + \sum_{\mu \neq \nu} a_{\mu \nu} (\chi_\mu \langle \chi_\nu | \chi_\tau \rangle + \chi_\nu \langle \chi_\mu | \chi_\tau \rangle)$$

$$+ \sum_{\mu \neq \nu} i b_{\mu \nu} (\chi_\mu \langle \chi_\nu | \chi_\tau \rangle - \chi_\nu \langle \chi_\mu | \chi_\tau \rangle) \quad (5.10)$$

by applying the definitions (5.6)–(5.8). Since $\langle \chi_\mu | \chi_\tau \rangle = \delta_{\mu \tau}$,

$$\Gamma_N \chi_\tau = p_\mu \chi_\mu + \sum_\mu (a_{\mu \tau} + a_{\tau \mu}) \chi_\mu + \sum_\mu i (b_{\mu \tau} - b_{\tau \mu}) \chi_\mu \quad (5.11)$$

after changing the summation indices $\nu$ and $\mu$. Using the symmetry properties $a_{\mu \tau} = a_{\tau \mu}$ and $b_{\mu \tau} = -b_{\tau \mu}$ we get

$$\Gamma_N \chi_\tau = p_\tau \chi_\tau + \sum_{\mu \neq \tau} 2(a_{\mu \tau} + ib_{\mu \tau}) \chi_\mu \quad (5.12)$$

and

$$\|\Gamma_N \chi_\tau\|^2 = p_\tau^2 + \sum_{\mu \neq \tau} 4(a_{\mu \tau}^2 + b_{\mu \tau}^2). \quad (5.13)$$
The right hand side of equation (5.13) can be identified as the total contribution of the state $\chi_\tau$ to the density matrix, whereas, according to the theorem mentioned previously, the left hand side disappears in the limit if $\chi_\tau$ becomes more and more detailed (or equivalently, becomes coarser).

Besides this result an even sharper statement was proved for the total contribution of $\chi_\tau$. Since $\Gamma_N$ is a positive operator, for any $N$-particle function $\phi$ $\langle \phi | \Gamma_N \phi \rangle \geq 0$. For fixed index sets $\mu$ and $\tau$, the particular choice $\bar{\phi} = c_\mu \chi_\mu + c_\tau \chi_\tau$ was taken. The condition $\langle \bar{\phi} | \Gamma_N \bar{\phi} \rangle \geq 0$ led to an essentially $2 \times 2$ matrix problem with a solution

$$4(a^2_{\mu\tau} + b^2_{\mu\tau}) \leq p_\mu p_\tau.$$  \hspace{1cm} (5.14)

Equality holds if $\Gamma_N$ is a pure state density operator. Applying (5.14) to (5.13) resulted in

$$p^2_\tau \leq \| \Gamma_N \chi_\tau \|^2 \leq p^2_\tau + \sum_{\mu \neq \tau} p_\mu p_\tau = p_\tau \sum_\mu p_\mu = p_\tau$$  \hspace{1cm} (5.15)

or

$$p_\tau \leq \| \Gamma_N \chi_\tau \| \leq \sqrt{p_\tau}$$  \hspace{1cm} (5.16)

and

$$4 \sum_{\mu \neq \tau} (a^2_{\mu\tau} + b^2_{\mu\tau}) \leq p_\tau (1 - p_\tau).$$  \hspace{1cm} (5.17)

Inequality (5.17) shows that the total contribution of the state $\chi_\tau$ in the density matrix is bounded by a single parameter $p_\tau = \langle \chi_\tau | \Gamma_N \chi_\tau \rangle$ which according to (5.16) approaches to zero in the infinitely detailed (or coarse) limit.

As the electron density $\rho(x) = N \gamma_1(x|x)$ is essentially the diagonal element of the one-electron density matrix, an expansion similar to (5.5) is applicable with the coefficients of $\gamma_1$. Consequently, the above results hold for the density, too, indicating the absence of extremely fine and rough structures in $\rho(x)$.

### 5.3 Reduction of degrees of freedom

Contraction (2.5) is a linear operation, thus its effect on the density matrix with expansion (5.5), can be treated separately to the expanding functions $A$, $B$ and $P$. The reduction of degrees of freedom for these functions results
5.3. Reduction of degrees of freedom

\[ \int A^{n_1,\ldots,n_N}_{m_1,\ldots,m_N}(x_1,\ldots,x_{N-1},x_N|x_1',\ldots,x_{N-1}',x_N)dx_N = \frac{1}{N} \sum_{i,j} (-1)^{i+j} \delta_{m_i,n_j} \times A^{n_1,\ldots,n_{i-1},n_{j+1},\ldots,n_N}_{m_1,\ldots,m_{i-1},m_{j+1},\ldots,m_N}(x_1,\ldots,x_{N-1}|x_1',\ldots,x_{N-1}') \]

\[ \int B^{n_1,\ldots,n_N}_{m_1,\ldots,m_N}(x_1,\ldots,x_{N-1},x_N|x_1',\ldots,x_{N-1}',x_N)dx_N = \frac{1}{N} \sum_{i,j} (-1)^{i+j} \delta_{m_i,n_j} \times B^{n_1,\ldots,n_{i-1},n_{j+1},\ldots,n_N}_{m_1,\ldots,m_{i-1},m_{j+1},\ldots,m_N}(x_1,\ldots,x_{N-1}|x_1',\ldots,x_{N-1}') \]

\[ \int P_{m_1,\ldots,m_N}(x_1,\ldots,x_{N-1},x_N|x_1',\ldots,x_{N-1}',x_N)dx_N = \frac{1}{N} \sum_{i} (-1)^{2i} P_{m_1,\ldots,m_{i-1},m_{i+1},\ldots,m_N}(x_1,\ldots,x_{N-1}|x_1',\ldots,x_{N-1}') , \quad (5.18) \]

where we have shortened the notations as \( A_{\mu\nu} = A_{\mu\nu}', B_{\mu\nu} = B_{\mu\nu}', a_{\mu\nu} = a_{\mu\nu}', b_{\mu\nu} = b_{\mu\nu}' \). We have found, that the contraction does not lead out of the space spanned by \( A \)-type basis functions of any electron number, nor from the spaces of functions that are to be expressed purely by \( B \) or purely by \( P \)-type expanding functions. Thus an \((N-1)\)-particle \( A \)-type function can be originated only from \( A \)-type functions of larger electron number \((N\) or greater), and \( B \) and \( P \) functions behave similarly. Expression (5.5) is then capable of describing not only pure state \( N \)-particle density matrices, but also ensemble ones, the difference lies only in the coefficients’ \( a_{\mu\nu}, b_{\mu\nu} \) and \( p_{\mu} \) arising in form (5.9) only in pure state case.

I have summarized one step of the contraction of a density matrix as

\[ \gamma_{N-1}(x_1,\ldots,x_{N-1}|x_1',\ldots,x_{N-1}') = N^{-1} \sum_{\mu\in\Omega_N} p_\mu \sum_{i} P_{m_1,\ldots,m_{i-1},m_{i+1},\ldots,m_N}(x_1,\ldots,x_{N-1}|x_1',\ldots,x_{N-1}') \]

\[ + N^{-1} \sum_{\mu\neq\nu\in\Omega_N} \sum_{i,j} (-1)^{i+j} \delta_{m_i,n_j} a_{m_1,\ldots,m_N} \times A^{n_1,\ldots,n_{i-1},n_{j+1},\ldots,n_N}_{m_1,\ldots,m_{i-1},m_{j+1},\ldots,m_N}(x_1,\ldots,x_{N-1}|x_1',\ldots,x_{N-1}') \]

\[ + N^{-1} \sum_{\mu\neq\nu\in\Omega_N} \sum_{i,j} (-1)^{i+j} \delta_{m_i,n_j} b_{m_1,\ldots,m_N} \times B^{n_1,\ldots,n_{i-1},n_{j+1},\ldots,n_N}_{m_1,\ldots,m_{i-1},m_{j+1},\ldots,m_N}(x_1,\ldots,x_{N-1}|x_1',\ldots,x_{N-1}') , \quad (5.19) \]
and of course, more of these steps can be executed one after another to get \( \gamma_p \), resulting in expressions like (5.5) with only \( p \) variables. Values \( p = 1 \) and 2 are of special interest, because they appear in the energy terms (4.10)–(4.12). From (5.5) the one- and two-electron density matrix can be written as

\[
\gamma_2(x_1, x_2 | x_1', x_2') = \sum_{\mu \in O_N} \frac{2!}{N!} \beta_\mu \sum_{i_1, i_2} P_{m_{i_1} m_{i_2}}(x_1, x_2 | x_1', x_2')
\]

\[
+ \sum_{\mu \neq \nu \in O_N} \sum_{i_1, i_2, j_1, \ldots, j_{N-2}} (-1)^{\sum_{k} i_k + j_k} \frac{2!}{N!} \delta_{m_{i_1}}^{n_{j_1}} \cdots \delta_{m_{i_{N-2}}}^{n_{j_{N-2}}} \times a_{m_{i_1}, \ldots, m_{N}}^{n_{j_1}, \ldots, m_{N}}(x_1, x_2 | x_1', x_2')
\]

\[
+ \sum_{\mu \neq \nu \in O_N} \sum_{i_1, i_2, j_1, \ldots, j_{N-2}} (-1)^{\sum_{k} i_k + j_k} \frac{2!}{N!} \delta_{m_{i_1}}^{n_{j_1}} \cdots \delta_{m_{i_{N-2}}}^{n_{j_{N-2}}} \times b_{m_{i_1}, \ldots, m_{N}}^{n_{j_1}, \ldots, m_{N}}(x_1, x_2 | x_1', x_2')
\]

(5.20)

\[
\gamma_1(x_1 | x_1') = \sum_{\mu \in O_N} \frac{1!}{N!} \beta_\mu \sum_{i} P_{m_i}(x_1 | x_1')
\]

\[
+ \sum_{\mu \neq \nu \in O_N} \sum_{i_1, \ldots, i_{N-1}, j_1, \ldots, j_{N-1}} (-1)^{\sum_{k} i_k + j_k} \frac{1!}{N!} \delta_{m_{i_1}}^{n_{j_1}} \cdots \delta_{m_{i_{N-1}}}^{n_{j_{N-1}}} \times a_{m_{i_1}, \ldots, m_{N}}^{n_{j_1}, \ldots, m_{N}}(x_1 | x_1')
\]

\[
+ \sum_{\mu \neq \nu \in O_N} \sum_{i_1, \ldots, i_{N-1}, j_1, \ldots, j_{N-1}} (-1)^{\sum_{k} i_k + j_k} \frac{1!}{N!} \delta_{m_{i_1}}^{n_{j_1}} \cdots \delta_{m_{i_{N-1}}}^{n_{j_{N-1}}} \times b_{m_{i_1}, \ldots, m_{N}}^{n_{j_1}, \ldots, m_{N}}(x_1 | x_1')
\]

(5.21)

These terms are so complicated, that they can not be used for checking \( N \)-representability.

### 5.4 Spin tracing

In order to be able to expand the energy terms in MRA basis, spin tracing is also necessary. The spin-traced two-particle density matrix can be expanded by the \( n \)th level scaling functions as

\[
\gamma_2^{[m]}(r_1, r_2 | r_1', r_2') = \sum_{k_1, k_2, \ell_1, \ell_2} \left[ g_{k_1 k_2}^{A,m} g_{k_1 k_2}^{B,m} (r_1, r_2 | r_1', r_2') \right]
\]

(5.22)
5.4. Spin tracing

where coefficients $g_{k_1k_2\ell_1\ell_2}^{A,B,m}$ are real numbers. The functions

$$\vartheta_{k_1k_2\ell_1\ell_2}^{A,m}(r_1, r_2| r_1', r_2') = \frac{1}{2} \left[ s_{mk_1}(r_1)s_{mk_2}(r_2)s_{m\ell_1}^*(r_1')s_{m\ell_2}^*(r_2') \\
+ s_{mk_2}(r_1)s_{mk_1}(r_2)s_{m\ell_2}^*(r_1')s_{m\ell_1}^*(r_2') \\
+ s_{m\ell_1}(r_1)s_{m\ell_2}(r_2)s_{mk_1}^*(r_1')s_{mk_2}^*(r_2') \\
+ s_{m\ell_2}(r_1)s_{m\ell_1}(r_2)s_{mk_2}^*(r_1')s_{mk_1}^*(r_2') \right] \quad (5.23)$$

and

$$\vartheta_{k_1k_2\ell_1\ell_2}^{B,m}(r_1, r_2| r_1', r_2') = \frac{i}{2} \left[ s_{mk_1}(r_1)s_{mk_2}(r_2)s_{m\ell_1}^*(r_1')s_{m\ell_2}^*(r_2') \\
+ s_{mk_2}(r_1)s_{mk_1}(r_2)s_{m\ell_2}^*(r_1')s_{m\ell_1}^*(r_2') \\
- s_{m\ell_1}(r_1)s_{m\ell_2}(r_2)s_{mk_1}^*(r_1')s_{mk_2}^*(r_2') \\
- s_{m\ell_2}(r_1)s_{m\ell_1}(r_2)s_{mk_2}^*(r_1')s_{mk_1}^*(r_2') \right] \quad (5.24)$$

are suitable to expand any density matrix $\gamma^A_2$. Functions $\vartheta_{A,B,m}$ meet symmetry properties (2.10) of $\gamma^A_2$

$$\vartheta_{k_1k_2\ell_1\ell_2}^{A,m}(r_1, r_2| r_1', r_2') = \vartheta_{k_1k_2\ell_1\ell_2}^{A,m}(r_2, r_1| r_2', r_1') \\
= \left( \vartheta_{k_1k_2\ell_1\ell_2}^{A,m}(r_1', r_2'| r_1, r_2) \right)^* \quad (5.25)$$

moreover the index symmetry,

$$\vartheta_{k_1k_2\ell_1\ell_2}^{A,m}(r_1, r_2| r_1', r_2') = \vartheta_{k_2k_1\ell_1\ell_2}^{A,m}(r_1, r_2| r_1', r_2') \quad (5.26)$$

$$\vartheta_{k_1k_2\ell_1\ell_2}^{B,m}(r_1, r_2| r_1', r_2') = \vartheta_{k_2k_1\ell_1\ell_2}^{B,m}(r_1, r_2| r_1', r_2') \quad (5.27)$$

but

$$\vartheta_{k_1k_2\ell_1\ell_2}^{A,B}(r_1, r_2| r_1', r_2') \neq -\vartheta_{k_2k_1\ell_1\ell_2}^{A,B}(r_1, r_2| r_1', r_2'). \quad (5.28)$$

The expansion coefficients $g$ can be derived from the coefficients in formula (5.5) for $N = 2$ as

$$g_{k_1k_2\ell_1\ell_2}^{A,m} = 2 \sum_{s_1s_2} a_{mk_1s_1, mk_2s_2; m\ell_1s_1, m\ell_2s_2} \quad (5.29)$$

and they have the following symmetries

$$g_{k_1k_2\ell_1\ell_2}^{A,m} = g_{k_2k_1\ell_1\ell_2}^{A,m} = g_{k_1k_2\ell_1\ell_2}^{A,m} \quad (5.30)$$
Tracing one of the space variables, the one-particle spin-traced density matrix can be written as

$$\gamma_1^{s[m]}(r|r') = \sum_{k,\ell} \left[ g_{k\ell}^{A,m} \vartheta_{k\ell}^{A,m}(r|r') + g_{k\ell}^{B,m} \vartheta_{k\ell}^{B,m}(r|r') \right],$$  \hfill (5.31)

where the expanding functions are

$$\vartheta_{k\ell}^{A,m}(r|r') = \frac{1}{2} \left[ s_{mk}(r)s_{m\ell}^*(r') + s_{m\ell}(r)s_{mk}^*(r') \right],$$  \hfill (5.32)

and

$$\vartheta_{k\ell}^{B,m}(r|r') = i \frac{1}{2} \left[ s_{mk}(r)s_{m\ell}^*(r') - s_{m\ell}(r)s_{mk}^*(r') \right].$$  \hfill (5.33)

Their symmetry properties are similar to those of the two-electron density matrices’ basis functions.

### 5.5 Density

The $m$th level approximation of the electron density arises by taking the diagonal element of (5.31)

$$\varrho^{[m]}(r) = \sum_{k,\ell} g_{k\ell}^{A,m} \vartheta_{k\ell}^{A,m}(r|r) + g_{k\ell}^{B,m} \vartheta_{k\ell}^{B,m}(r|r).$$  \hfill (5.34)

In the frequent case, if the scaling functions are real, \( \varrho_{k\ell}^{B,m}(r|r') = 0 \), which leads to

$$\varrho^{[m]}(r) = \sum_{k,\ell} g_{k\ell}^{A,m} s_{mk}(r)s_{m\ell}(r).$$  \hfill (5.35)

It is important to realize, that if the supports of the scaling functions do not overlap, i.e., if \(|k - \ell| > N_s\), the product \( s_{mk}(r)s_{m\ell}(r) \) will be zero, thus the coefficient \( g_{k\ell}^{A,m} \) does not count in the expansion of the density, nor to that of the kinetic or external potential energy functionals, thus it can be chosen arbitrarily.

Note, that the products \( s_{mk}(r)s_{m\ell}(r) \) do not constitute a basis of the density in the strict mathematical sense. It may be possible, that more $m$th level expansions, with different sets of coefficients \( g_{k\ell}^{A,m} \) exist for one given density.

### 5.6 Energy terms

With such expansion of the density matrices the kinetic (4.10), the electron-electron interaction (4.11) and the external potential energy (4.12) can be...
5.6. Energy terms

written by lengthy but straightforward algebraic calculations, applying the
dilation and translation properties of the scaling functions as

\[
\langle \hat{T} \rangle^{[m]} = \frac{1}{2} \sum_{k\ell} g_{k\ell}^{A,m} T_m(k - \ell) \tag{5.36}
\]

\[
\langle \hat{W} \rangle^{[m]} = \sum_{k_1k_2\ell_1\ell_2} g_{k_1k_2\ell_1\ell_2}^{A,m} W_m(k_1 - \ell_1, k_2 - \ell_2, k_1 - k_2) \tag{5.37}
\]

\[
\langle \hat{V} \rangle^{[m]} = \sum_{\alpha} Z_\alpha \sum_{k\ell} g_{k\ell}^{A,m} V_m(2^{-m}k - R_\alpha, 2^{-m}\ell - R_\alpha) \tag{5.38}
\]

with the expansion coefficients \( g_{k\ell}^{A,m} \) and \( g_{k_1k_2\ell_1\ell_2}^{A,m} \) of the one and two-electron
density matrix. \( Z_\alpha \) is the \( \alpha \)th atom’s atomic number and \( R_\alpha \) is its coordinate. The functions covered by the calygraphical letters can be originated

\[
T_0(k) = \int s'_{00}(r) s'_{0k}(r) \, dr, \tag{5.39}
\]

\[
W_0(k, \ell, j) = \int \frac{s_{00}(r_1) s_{00}(r_2) s'_{0k}(r_2) s'_{0\ell}(r_1)}{|r_1 - r_2 - j|} \, dr_1 \, dr_2, \tag{5.40}
\]

\[
V_0(q_1, q_2) = \int \frac{s_{00}(r - q_1) s'_{00}(r - q_2)}{|r|} \, dr, \tag{5.41}
\]

where \( s'(r) = dx(r)/dr \). The zero index means that these functions belong
to \( m = 0 \). For higher resolution levels \( m \) the values can be derived from
\(5.39\), \(5.40\) and \(5.41\) as \( T_m = 2^m T_0 \), \( W_m = 2^{2m} W_0 \) and \( V_m = 2^m V_0 \),
respectively. According to these results energy functionals can be expanded
through three types of universal functions. Due to the compact support of
scaling functions the overlap in expressions \(5.39\)-\(5.41\) is zero for most values
of the arguments. Function \( T \) is defined for one integer variable, making
it especially simple to manage, as it represents a series of few numbers for
the arguments \( |k| < N_s \). Similarly, \( W \) is to be calculated on an integer
grid of three variables with the constraint \( |k|, |\ell| < N_s \). The numerical
storage of its values is much easier than the similar problem of storing two-
electron integrals in usual numerical approaches. Moreover, since they do
not depend on the actual system properties, only on the type of wavelets,
the values of \( T \) and \( W \) can be calculated and organized to databases. The
universal function \( V \) is significant for the real values \( |q_1 - q_2| < N_s \) and
zero outside of this range. Since the interaction with the external potential
is a functional of the density with the well known shape \(4.12\), it is not
necessary to express it this way. All these advantageous properties offer the
possibility of a calculating method of \( O(N) \).
Chapter 6

One-electron density matrices resulting in a prescribed electron density

6.1 Approximation of the electron density at resolution level $m$

As definition (4.9) requires the construction of density matrices which correspond to a fixed density $ρ(r)$ we have studied the question of approximating a preselected electron density by an $m$th level scaling function expansion. I will give here an MRA expansion for inhomogeneous bosonic and fermionic systems’ one-electron density matrix.

As the scaling functions known and widely used in the literature are real, in the following consideration we will assume $s_{mℓ} = s^*_m$, yielding all $ψ_{kℓ}^m = 0$. We will also assume that the scaling functions are compactly supported.

According to this fact for homogeneous density $ρ(r) = ρ_0$ the $m$th level expansion of form (5.34) easily follows from the partition of unity (1.13) by choosing

$$g_{kℓ}^{A,m} = 2^{-m}ρ_0.$$

This means, that the homogeneous density is exactly reproducible at any resolution levels $m$, which was a good motivation for continuing this project.

Since the density is never negative and $\int ρ(r)dr = N$, its root, $\sqrt{ρ(r)}$ is in $L^2(\mathbb{R})$, and it can be approximated at resolution level $m$ as

$$\sqrt{ρ}^m(r) = \sum_k c_k^m s_{mk}(r),$$

with the coefficients

$$c_k^m = \int \sqrt{ρ}(r)s_{mk}(r)dr.$$
Applying an integral mean value theorem, and $\int s_{mk}(r)dr = 2^{-m/2}$, we get

$$c^m_k = \sqrt{\varrho}(\xi) \int s_{mk}(r)dr = 2^{-m/2} \sqrt{\varrho} \left(2^{-m}(k + \eta)\right).$$  \hspace{1cm} (6.4)

The argument of $\sqrt{\varrho}$ is in the support of the scaling function $s_{mk}$, thus $\xi \in 2^{-m}[k, k + 1)$, and for the parameter $\eta$ holds, that $0 \leq \eta < N_s$.

Substituting (6.4) into the Eq. (6.2), the density’s $m$th level expansion will have the form (5.35) with the expansion coefficients

$$g^{A,m}_{k\ell} = 2^{-m/2} \sqrt{\varrho} \left(2^{-m}(k + \eta)\right) \sqrt{\varrho} \left(2^{-m}(\ell + \eta)\right).$$  \hspace{1cm} (6.5)

I would like to emphasize, that while for the expansion (6.2) of $\sqrt{\varrho}$ all the coefficients are necessary, in Eq. (5.35) only those coefficients $g^{A,m}_{k\ell}$ are relevant, for which $|k - \ell| < N_s$. The other coefficients can be chosen arbitrarily, as it was mentioned at the end of Sec. 5.5.

In order to examine the convergence of the method, I have carried out numerical calculations for slowly, and rapidly varying densities with the scaling function set Daubechies-4. For this set $N_s = 3$, and if the expansion coefficients are arranged in a matrix $G_{k\ell} = g^{A,m}_{k\ell}$, only its diagonal and first two off-diagonal elements are essential for reproducing the density. I have taken a Gaussian function $\exp(-r^2/2\sigma)$, with $\sigma = 3$ as a typical slowly varying function. The zero level approximation is surprisingly good, considering the fact, that the width of the Gaussian is only twice the support of the scaling functions $s_{0k}$. The second level expansion is also shown Fig. 6.1. The unexpectedly small error of such slowly varying functions can be attributed to the vanishing first moment of the Daubechies-4 set, which fact was mentioned previously, in Sec. 1.5. Application of coiflets would improve the results.
I return now to the question, how the \( m \)th level representation of a density \( \rho^m(r) \) determines the corresponding \( m \)th level expansion of \( \gamma_1^s \). As I have mentioned previously (for real scaling functions) the values of \( g_{k\ell}^{B,m} \) do not affect \( \rho^m(r) \), nor do the values of \( g_{k\ell}^{A,m} \) with \( |k - \ell| \geq N_s \). This provides a considerable freedom in choosing \( \gamma_1^s \) which are compatible with the given \( m \)th level approximation of the density.

As we have seen the scaling function expansion (5.35) with the coefficients (6.5) reproduces a preselected electron density extremely well even at a moderate refinement level. Using coefficients (6.5) in the expansion

Figure 6.2: Density expansion (5.35) of a model density of the carbon monoxide molecule (dotted line) at resolution levels \( m = 0 \), \( m = 3 \) and \( m = 6 \). For the expansion coefficients we have applied equation (6.5). The insets illustrate the scaling functions \( s_{00}(r) \), \( s_{30}(r) \) and \( s_{60}(r) \), respectively. Note, that the scales of the insets and the molecular density are not comparable for technical reasons. Also, the proportions of the vertical and horizontal dimensions of the scaling functions are not exactly realistic. Atomic units were used.

Rapidly varying densities occur typically at nuclear cusps. In order to test our approach for real molecular systems I have approximated the one-dimensional intersection of a model density of the carbon monoxide molecule. The molecular density is estimated as a sum of the atomic densities of the individual oxygen and carbon atoms calculated according to Slater’s rule [83]. The results of the calculations in Fig. 6.2 show that the applied expansion method results in a considerably good approximation even in the neighborhood of the nuclear cusps. It can also be realized, that the regions far from the cusps are described extremely well even at low resolution levels. For studying the errors around the nuclei I have plotted the difference between the approximated model density and the approximating function (5.35) in Fig. 6.3. Easy to see, that around the cusps the magnitude of the error decreases, and the intervals with visible error shorten exponentially with increasing resolution level \( m \).
(5.31) defines a spin-traced one-particle density matrix $\gamma_1^s$, as well. It may be possible, however, that such a density operator does not correspond to any real physical system with fermionic particle statistics, i.e., it is not $N$-representable. According to the generalized Pauli principle \[82], mentioned in section 4.2, $\gamma_1$ is $N$-representable if all of its eigenvalues (i.e., the natural occupation numbers) satisfy the condition $0 \leq n_i \leq 1$. It is clear that the eigenvalue problem

$$\int \gamma_1^s(r|r')\varphi(r')dr' = n\varphi(r)$$

(6.6)

is equivalent to that of the matrix $g^{A,m}_{k\ell}$

$$\sum_{\ell} g^{A,m}_{k\ell} a^{m}_{\ell} = na_{k}^{m}$$

(6.7)

where the natural orbitals $\varphi(r) = \sum_{\ell} a^{m}_{\ell} s_{m\ell}(r)$.

Let us consider the eigenvalue problem

$$Ga = na$$

(6.8)

where the matrix elements of $G$ are defined according to (6.3) and (6.5) as $G_{k\ell} = g^{A,m}_{k\ell} = c^m_{k} c^m_{\ell}$. Straightforward calculation leads to the result, that one of the eigenvectors of problem (6.8) $a = c$ with the eigenvalue $n = \text{Tr} G$. Here, we have introduced the vector notation $c = (c^m_{k})$. All other eigenvectors are orthogonal to $c$ and belong to the eigenvalue zero. As according to Löwdin’s normalization $n = \text{Tr} G = \text{Tr} \tilde{\Gamma}_1 = N$, it is clear that each particle of the system occupies the natural orbital $a = c$, i.e.,
6.2. Particle statistics and $N$-representability

the density matrix defined by the matrix elements (6.5) corresponds to a Bose condensate. Consequently, the definition (6.5) has to be modified in order to describe a fermionic system properly. Note, that the discussed approximation corresponds to the $m$th level expansion of the Weizsäcker-type density operator $\gamma^s_W(r|r') = \varrho^{1/2}(r)\varrho^{1/2}(r')$.

An obvious possibility for creating an $N$-representable fermionic one-particle density matrix is to apply the Macke-Harriman construction [84, 85] of orthogonal one-particle orbitals, each belonging to the same density function. For any integer $K$ the orbital

$$\varphi_K(r) = \left(\frac{\varrho(r)}{N}\right)^{1/2}e^{iKf(r)+\phi(r)},$$

results in the one-particle density $\varrho(r)/N$. For any index pairs $K$ and $K'$

$$\langle \varphi_K | \varphi_{K'} \rangle = \delta_{KK'}$$

if

$$f(r) = 2\pi \frac{N}{r} \int_{-\infty}^{r} \varrho(x)dx$$

and $\phi(r)$ is an arbitrary phase function. It is evident that a Slater determinant built from $N$ orbitals with different $K$ values gives the requested total density $\varrho(r)$. The same $N$-particle wave function can be used to calculate the $N$-representable one-particle density matrix

$$\gamma^s_{1MH}(r|r') = \sum_{K} \varphi_K(r)\varphi^*_K(r')$$

$$= \frac{1}{N} \sqrt{\varrho(r)\varrho(r')}e^{i[\phi(r)-\phi(r')]} \sum_{K} \left(e^{i(f(r)-f(r'))}\right)^K.$$  

Choosing

$$\phi(r) = -\frac{N-1}{2}f(r)$$

and the index set $K = 0, \ldots, N-1$ we arrive at

$$\gamma^s_{1MH}(r|r') = \frac{1}{N} \sqrt{\varrho(r)\varrho(r')} \frac{\sin\frac{N}{2}(f(r)-f(r'))}{\sin\frac{1}{2}(f(r)-f(r'))}.$$  

Translating the formula (6.13) to the scaling function representation we will select the sampling sites $r = 2^{-m}(\ell + \eta)$ and $r' = 2^{-m}(k + \eta)$. For $N = 1$ all (bosonic) formulae elaborated in the previous section are applicable to the fermionic case, as well. Thus, according to (6.5) $\varrho(r) = 2^m g_{\ell\ell}^{A,m}$ and $\varrho(r') = 2^m g_{kk}^{A,m}$. On the other hand, for $N = 1$ from (6.13) we have

$$\gamma^s_{1MH}(r|r') = \sqrt{\varrho(r)\varrho(r')} = 2^m \sqrt{g_{kk}^{A,m} g_{\ell\ell}^{A,m}} = 2^m g_{k\ell}^{A,m}$$

where the last equation follows from (6.5). From these considerations naturally arises the generalized definition

$$g_{k\ell}^{A,m} = 2^{-m} \gamma^s_{1}(2^{-m}(\ell + \delta)|2^{-m}(k + \delta))$$
yielding

\[ g_{k\ell}^{A,m} = \frac{1}{N} \sqrt{g_{kk}^{A,m} g_{\ell\ell}^{A,m}} \cdot \frac{\sin \frac{N}{2} (f(2^{-m}(\ell + \delta)) - f(2^{-m}(k + \delta)))}{\sin \frac{1}{2} (f(2^{-m}(\ell + \delta)) - f(2^{-m}(k + \delta)))}, \tag{6.16} \]

using expression (6.13). I have calculated the electron density resulting from expansion (5.34) with the coefficients (6.16) for the slowly varying Gaussian model density used previously. As we see in Fig. 6.4, the Fourier-type orbitals (6.9) lead to a crude approximation at low resolution levels, although convergence is excepted as \( m \to \infty \). Unfortunately, the convergence rate is relatively low, showing that the representation of the delocalized Fourier-type orbitals (6.9) by localized scaling functions is inadequate from the practical point of view.

### 6.3 Inclusion of electron correlation

Although, the Macke-Harriman construction leads to an \( N \)-representable density operator, \( \gamma_{1,\text{MH}}^{\text{r}} \) corresponds to an independent particle approximation. As the role of electron correlation in large electron systems is widely known, we have studied the question, how correlation appears in scaling function expansions based on my supervisor’s idea. The dissociation error of the restricted Hartree-Fock (RHF) method can be illustrated by the model example of two well separated, non-interacting H atoms. The physically inappropriate RHF wave function describes both electrons evenly distributed among the two atoms. For a heuristic consideration, let the atoms be situated at the positions \( R = 2^{-m}\ell \) and \( R = 2^{-m}k \), and have the ”1s” orbitals \( s_{m\ell} \) and \( s_{mk} \), thus the RHF MOs are

\[ \varphi_{\uparrow}(\mathbf{x}) = 2^{-1/2}[s_{m\ell}(\mathbf{x}) + s_{mk}(\mathbf{x})], \]

\[ \varphi_{\downarrow}(\mathbf{x}) = 2^{-1/2}[s_{m\ell}(\mathbf{x}) + s_{mk}(\mathbf{x})]. \tag{6.17} \]
6.3. Inclusion of electron correlation

The spin dependent one-electron density matrix with occupation numbers 1 and 1 for up and down spins is

\[ \gamma_1(\mathbf{x}|\mathbf{x}') = \varphi_1(\mathbf{x})\varphi_1^*(\mathbf{x}') + \varphi_1(\mathbf{x})\varphi_1^*(\mathbf{x}') . \] (6.18)

Using (6.17) and after spin-tracing we arrive at

\[ \gamma_s^1(r|r') = s_{m\ell}(r)s_{m\ell}(r') + s_{mk}(r)s_{mk}(r') + s_{mk}(r)s_{mk}(r') \] (6.19)

showing, that \( g^{A,m}_{k\ell} = g^{A,m}_{\ell \ell} = g^{A,m}_{kk} = 1 \) and \( g^{B,m}_{k\ell} = g^{B,m}_{\ell \ell} = g^{B,m}_{kk} = 0 \). On the other hand, the proper arrangement of electrons corresponds to the unrestricted Hartree-Fock (UHF) solution with two separated electrons on the atoms

\[ \varphi_1(\mathbf{x}) = s_{m\ell}(\mathbf{x}) \]
\[ \varphi_1(\mathbf{x}) = s_{mk}(\mathbf{x}) . \] (6.20)

Calculating the spin traced one-electron density matrix as above we get

\[ \gamma_s^1(r|r') = s_{m\ell}(r)s_{m\ell}(r') + s_{mk}(r)s_{mk}(r') \] (6.21)

or \( g^{A,m}_{k\ell} = 0 \) and \( g^{A,m}_{\ell \ell} = g^{A,m}_{kk} = 1 \). Note, that the eigenvalues of the RHF-type matrix \( \gamma_s^1 \) are 2 and 0, whereas the UHF-type eigenvalues are 1 and 1.

This model leads to the general assumption that those 1-matrices \( \gamma_s^1 \), which reflect electron correlation correctly should have the property

\[ g^{A,m}_{k\ell} \rightarrow 0 \text{ for large } |k - \ell|. \] (6.22)

This recognition shows that for correlated systems expression (6.5) fails for large index differences \( |k - \ell| \). Furthermore, the well known limiting behavior [86, 87]

\[ \gamma_s^1(r|r') \xrightarrow{r,r' \to \infty} \gamma_{1W}^s(r|r') \] (6.23)

is valid only if \( r \) and \( r' \) approach infinity simultaneously, i.e. if \( |r - r'| \) remains small.

The above discussed procedures of constructing one-particle density matrices for a prescribed electron density are either bosonic or independent particle approximations. We have shown, that an approach using local arguments of my supervisor, leads to a one-electron density matrix, which is correlated, i.e. fulfills (6.22), \( N \)-representable in the infinite resolution limit and at the same time conserves the excellent quality density of the bosonic construction. As I have mentioned previously, most elements of \( \gamma_s^1 \) are irrelevant in respect of expanding \( \varrho(r) \). In the following considerations certain elements of matrix \( G \) will be set to zero instead of using expression
CHAPTER 6. ONE-ELECTRON DENSITY MATRICES

I will summarize below, how the zero elements of matrix $G$ should be selected.

Let us divide the space into non-overlapping regions, using the local nature of the scaling functions. A set of scaling function indices which characterizes a given region of the space is denoted by $I_i \subset \mathbb{Z}$. The following properties of the index set are demanded. $I_i \cap I_j = \emptyset$ if $i \neq j$, and $\bigcup_{i=1}^{N} I_i = \mathbb{Z}$, where $N$ is chosen by $N = \int_{-\infty}^{\infty} \sigma(r)dr \in \mathbb{N}$, thus sets $I_i, i = 1, \ldots, N$ cover the entire scaling function index space. We have introduced the truncated matrix $G'$ with the elements

$$G'_{k\ell} = \begin{cases} 0 & \text{if } k \in I_i, \ell \in I_j, i \neq j, \\ \left(g_{k,k}^{A,m} g_{\ell,\ell}^{A,m}\right)^{1/2} & \text{if both } k \text{ and } \ell \in I_i. \end{cases}$$  \hspace{1cm} (6.24)

As an illustration the structure of blocks of $G'$ is shown here if $N = 2$ and $I_1$ and $I_2$ are disjoint intervals.

$$G' = \begin{pmatrix} G^{(1)} & 0 \\ 0 & G^{(2)} \end{pmatrix}$$

Similarly to the bosonic case, the eigenvectors of $G'$ with non-zero eigenvalues are clearly $c^{(1)}$ and $c^{(2)}$, where

$$c^{(i)}_k = \begin{cases} c^m_k & \text{if } k \in I_i, \\ 0 & \text{otherwise}. \end{cases} \hspace{1cm} (6.25)$$

The corresponding eigenvalues are

$$\eta^{(i)} = \sum_{k \in I_i} G_{kk}. \hspace{1cm} (6.26)$$

All other eigenvectors belong to the eigenvalue zero, and follow the block structure of matrix $G'$ as $a = (a^{(1)},0)$ or $a = (0,a^{(2)})$, where $a^{(1)} \perp c^{(1)}$ and $a^{(2)} \perp c^{(2)}$. The expression (6.26) shows that a one-particle density matrix expanded by (5.31) using the matrix elements of $G'$ as expansion coefficients, satisfies the generalized Pauli principle to a good approximation, if the index sets $I_i$ are chosen in such manner, that the values of the summations in (6.26) give unity as precisely as possible.

The generalization of the above procedure to arbitrary $N$ is trivial. In Fig. 6.5 I have illustrated, how a density matrix generated as outlined above satisfies the generalized Pauli principle. I have calculated the coefficients $g_{k\ell}^{A,m}$, then filled up the matrix $G'_{k\ell}$ until the sum (6.26) did not reach 1,
when I have started a new block and repeated the procedure. At the end, the eigenvalues of matrix $G_{k\ell}$ were calculated. The error of the resulting non-zero eigenvalues disappears exponentially as $m \to \infty$. I have also plotted the density arises according to (5.34) in Fig. 6.6, using the expansion coefficients (6.24). Although the range of considerable deviations decreases with increasing resolution, unfortunately the amplitude of the error compared to the required $g(r)$ remains constant.

Figure 6.5: The deviation from their ideal value of the trace of blocks of $G'$ which belongs to the six-particle density shown in Fig. 6.1 as a function of the resolution level $m$. Atomic units were used.

Figure 6.6: Expansion (5.34) of the slowly varying 6-particle Gaussian density of Fig. 6.1 using the matrix elements of $G'$ as expansion coefficients at resolution levels $m = 2$ and $m = 4$. Atomic units were used.

In order to avoid this unsatisfactory behavior we have slightly modified the definition of $G'$. I recall, that for the Daubechies-4 scaling function only the first and second off-diagonal elements of the matrix $g^{A,m}_{k\ell}$ affect the value of the density. This leads to the natural assumption, that completing the zero blocks of $G'$ by the necessary first and second off-diagonal elements according to (6.5) results in an excellent $g(r)$ approximation, and at the same time $N$-representability is retained in the $m \to \infty$ limit. For $N = 2$
Figure 6.7: The deviation from the limits of the eigenvalues of the density matrix originated from the Gaussian density of Fig. 6.2, calculated according to $G''$, as a function of the resolution level $m$. The symbols $\circ$ and $+$ denote the deviation of the eigenvalues tending to 1, the others ($\times$, $\diamond$, $\ast$, and $\square$) tending to zero. Atomic units were used.

The matrix of coefficients looks like the following diagram

$$G'' = \begin{pmatrix} G^{(1)} & 0 \\ 0 & G^{(2)} \end{pmatrix}$$

Two other off-diagonal elements are introduced, they do not influence the resulting density, and my numerical observations have shown, that $G''$ leads to faster convergence in the eigenvalues. The density produced by $G''$ is the same as in the bosonic case (see e.g. Fig. 6.1 or 6.2).

Regarding $N$-representability, we have considered the case $N = 2$. It can be proved, that all but six eigenvalues of $G''$ are exactly zero. As Fig. 6.7 shows, two of the non-zero eigenvalues converge exponentially to unity, and the remaining four tend to zero at the fine resolution limit.

By the construction of $G''$ it is clear that the diagonal, first and second off-diagonal elements of the matrix are the same as those of the Weizsäcker-type density operator. According to my previous note in Sec. 5.5, these are the terms which determine the kinetic energy expectation value, thus we conclude that $G''$ corresponds to a density matrix which is correlated, satisfies the Pauli-principle in $m \to \infty$ limit, but at the same time yields the Weizsäcker kinetic energy term. This result shows that presence of the
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‘statistical’ correction $\tilde{\gamma}$ in the factorization [88]

$$\gamma_1^s(r|r') = \gamma_1^{s,W}(r|r') \tilde{\gamma}(r|r')$$ (6.27)

can not be attributed purely to the exchange effects.
CHAPTER 6. ONE-ELECTRON DENSITY MATRICES...
Chapter 7

Adaptive refinement of the MRA-expansion

Although, the calculation of the energy expectation values is reduced to using few numerical values of functions $T$, $W$ and $V$, it is clear, that keeping the number of expanding basis functions as low as possible is essential in practical applications. As I have mentioned in Sec. 1.4, increasing the resolution level uniformly over the whole system to $m_1$ results in an exponential increase in the number of basis functions. Obviously, such refinement is useless in most parts of the system, the finest resolutions are necessary only in the most detailed regions, especially around the nuclei.

As the electron density $\varrho$ is the principal quantity in DFT calculations, naturally has arisen the question, how many consecutive refinement steps were necessary in order to represent a function in the bilinear forms (5.31) and (5.35). Of course we have expected, that owing to the uneven distribution of the details, the necessary resolution level was locally different for an appropriate precision. To investigate this problem I have introduced a local refinement method based on the pyramid algorithm.

According to the results of the previous chapter, the bilinear representation of the electron density can be easily reduced to a classical basis function expansion of $\sqrt{\varrho}(r)$ in the space $L^2(\mathbb{R})$, using the identity $\varrho(r) = \sqrt{\varrho(r)} \sqrt{\varrho(r)}$. As the function $\sqrt{\varrho}(r)$ is square integrable ($\int \varrho = N$), its $m_1$th level expansion gives

$$\sqrt{\varrho}^{[m_1]}(r) = \sum_k c_{m_1k} s_{m_1k}(r) \quad \text{with} \quad c_{m_1k} = \langle s_{m_1k} | \sqrt{\varrho} \rangle,$$

or equivalently

$$\sqrt{\varrho}^{[m_1]}(r) = \sum_k c_{m_0k} s_{m_0k}(r) + \sum_{m=m_0}^{m_1-1} \sum_k d_{mk} w_{mk}(r).$$

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Here we have used the fact, that the subspace $V_{m_1}$ is spanned both by the basis function set $\{s_{m_1 k} | k \in \mathbb{Z}\}$ and $\{s_{m_0 k}, w_{mk} | k \in \mathbb{Z}, m = m_0, \ldots, m_1 - 1\}$, respectively. The bilinear form of $g^{(m)}(r)$ is achieved as a square of Eq. (7.1) or (7.2). The previous chapter was about Eq. (7.1). The wavelet expansion formula (7.2) offers the opportunity, to apply local refinements in those regions of the space, where the error of the approximation is not tolerable. In this procedure the locality (compact support) of the basis functions plays an essential role. The summation for the wavelets is restricted for those $k$ indices, where the support of the wavelet $w_{mk}$ lies in the large error regions, and the numerical realization is also based on this fact.

For a numerical study, we have divided the molecule into regions bearing different detail characteristics of the density. The most problematic parts of the density are the surroundings of the nuclei, where sharp exponential peaks appear due to the nuclear cusps. We have hoped, however, that since the wavelet expansions were surprisingly effective in the analysis of point singularities, the nuclear cusps could have been described reasonably by MRA. We have not expected too much trouble in expanding the asymptotic tails of the density, far from the nuclei and chemical bonds. The description of the bonding regions by wavelet expansions has not been obvious at the first sight, because of the lack of proper model density. In order to study the detail peculiarities we have introduced different models for the domains mentioned above, guided by the idea of my supervisor.

### 7.1 Local error measure

In order to be able to decide whether further refinement of the approximation is necessary in the given region of space, an appropriate local method is required for measuring the deviation of the approximated function and its MRA expansion. Integral-type error bounds, like the deviation in the total energy [57] or norm of the difference function, are not satisfactory in this respect. An other drawback of total energy error measure is the well known fact following from straightforward considerations, that the error in the wave function $\delta \Psi$ appears only in the second order in the total energy. This can cause a misleading conclusion about an acceptable $\delta \Psi$ provided that $\delta E \sim (\delta \Psi)^2$ is small. In order to avoid these difficulties we have applied local deviation error criteria, which are mathematically much stricter than global or integral conditions.

Since the representation of the density matrices is strongly connected to that of $g(r)$ (see [89]–[91], or chapter 6), we have focused our interest on the MRA representation of the electron density. There are known approximations of $g$ in the nuclear and asymptotic regions of the molecules, unfortunately, this is not the case in the bonding areas. In these domains the one-electron wave functions are better known objects, and we have com-
pared the wave function with its MRA approximation. In order to have compatible error conditions in all three regions of the molecule, we have checked the deviation of \( \sqrt{\varrho} \) and its approximation in the cusp and asymptotic domains. In principle, a pointwise convergence criterion is satisfied if condition
\[
|\sqrt{\varrho^{(m)}}(r) - \sqrt{\varrho}(r)| \leq \delta \quad \text{or} \quad |\Psi^{(m)}(r) - \Psi(r)| \leq \delta \tag{7.3}
\]
holds for some \( \delta \). We have applied different values of \( \delta_d \) in different domains \( D \) of the molecule, chosen according to appropriate physical considerations.

In practice, at a given resolution level \( m \) I have divided the studied domain \( D \subset \mathbb{R} \) into intervals \( I_{mk} = 2^{-m}[k, k + 1) \) for \( 2^{-m}k \in D \), where I have calculated
\[
\max_{r \in I_{mk}} |\sqrt{\tilde{\varrho}(r)} - \sqrt{\varrho}(r)| = M_{mk} \quad \text{or} \quad \max_{r \in I_{mk}} |\Psi^{(m)}(r) - \Psi(r)| = M_{mk}. \tag{7.4}
\]
If \( M_{mk} < \delta_d \) held, I have considered the approximation at level \( m \) to be sufficient and have omitted \( w_{mk} \) at the next refinement step. If this condition did not hold, I have included \( w_{mk} \) in the approximation, leading to an \( m + 1 \) level expansion in the interval \( I_{mk} \). This procedure has been repeated for all the intervals and for finer and finer resolutions until no interval was found to be refined.

### 7.2 Asymptotic domain

The radial part of the density in the asymptotic domain
\[
\varrho(r) \approx A^{wa} r^{2\gamma - 1} \exp(-2\sqrt{2I_{\text{min}}} r) \tag{7.5}
\]
is determined by the most diffuse natural orbital [92]. Here \( I_{\text{min}} \) is the least ionization energy and \( \gamma = \sum a Z_a / \sqrt{2I_{\text{min}}} \). The summation runs on all atomic numbers of the system. In our model calculations the radial part of the asymptotic density of various atoms has been approximated using the MRA expansion (7.2), thus the originally three dimensional problem reduced to one dimension. As the behavior far from the nucleus is due to one natural orbital, we have chosen the constant \( A^{wa} \) to assure 3D normalization \( \int 4\pi r^2 \varrho = 1 \). We have defined the range of the asymptotic domain as \( D_{\text{as}} = [r_a, \infty) \), where \( r_a \) is the covalent atomic radius.

A physical consideration leading to an appropriate error bound \( \delta_{\text{as}} \) is based on the experimental error bars of ionization energies. I have chosen
\[
\delta_{\text{as}} = \max_{r \in D_{\text{as}}} |\sqrt{\tilde{\varrho}(r) - \sqrt{\varrho}(r)|, \tag{7.6}
\]
where \( \tilde{\varrho} \) is calculated according to (7.5) with a modified value of the ionization energy \( \tilde{I}_{\text{min}} = I_{\text{min}}(1 \pm 0.001) \). This resulted in \( 10^{-5} \leq \delta_{\text{as}} \leq 6 \times 10^{-5} \), except for hydrogen and helium, with \( \delta_{\text{as}} \approx 3.3 \times 10^{-4} \).
I have taken the values of \( r_a \) and \( I_{\text{min}} \) from standard periodic tables. In the cases of H and He expression (7.5) led to a density function concentrated close to the nucleus, and in this sense it did not correspond to a real asymptotic behavior. As a matter of fact, the description of the density around the nuclei has been considered at the treatment of nuclear cusps. Thus, the MRA expansion of the asymptotic decay of the density was calculated for the atoms \( Z = 3, \ldots, 18 \). The result of the calculations has shown, that already very limited refinement of the wavelet basis set is capable to reproduce formula (7.5) within the chosen error bounds. This finding can be attributed to the previously mentioned fact, that slowly varying (almost constant) functions are extremely well representable due to (1.13).

It has turned out, that the necessary grid length was \( 2^{-2} \text{ a.u.} \) (corresponding to resolution level \( m = 2 \)) for the atoms boron, nitrogen, fluorine and neon, \( 2^{-1} \text{ a.u.} \) (\( m = 1 \)) for the other atoms in the first row of the periodic table and for \( Z = 17 \) and 18. The \( m = 0 \) level approximation, leading to the grid length 1 a.u., was already satisfactory for heavier atoms \( Z = 11, \ldots, 16 \). According to these result we have suggested a starting resolution level of \( m_0 = 1 \), or of grid length 0.5 a.u.

### 7.3 Bonding regions

Modeling the density between the atoms in the bonding regions was not trivial, as no explicit approximations existed in this domain. Thus, for studying the precision of MRA expansions, we have followed a different strategy. From broad computational experiences we learned that the atomic basis function sets describe chemical bonds appropriately. One of the most popular sets is 6-31G*, and we have studied the representation of the 1D radial cut of the valance shell atomic orbitals, as well as that of the polarization functions. The split valance shell atomic orbitals contain contracted s and p functions with the radial parts

\[
R_s(r) = d_1^s g^s(\alpha_1, r) + d_2^s g^s(\alpha_2, r) + d_3^s g^s(\alpha_3, r), \\
R_p(r) = d_1^p g^p(\alpha_1, r) + d_2^p g^p(\alpha_2, r) + d_3^p g^p(\alpha_3, r),
\]  

(7.7)

where the normalized 3D primitive Gaussians are defined as \( g^s(\alpha, r) = A^s(\alpha) \exp(-\alpha r^2) \) and \( g^p(\alpha, r) = A^p(\alpha) r \exp(-\alpha r^2) \) with the normalization constants \( A^s(\alpha) = (2\alpha/\pi)^{3/4} \) and \( A^p(\alpha) = (2^7\alpha^5/(3^2\pi^3))^{1/4} \). The contraction coefficients \( d_k^{s,p} \) and the exponents \( \alpha_k \) are tabulated in Ref. [30]. The uncontracted atomic basis functions are defined similarly, with \( d_1^{s,p} = 1 \) and \( d_2^{s,p}, d_3^{s,p} = 0 \), and with properly selected exponents. The polarization functions are uncontracted d-type Gaussian orbitals with the radial part \( g^d(\alpha, r) = A^d(\alpha) r^2 \exp(-\alpha r^2) \), where \( A^d(\alpha) = (2^11\alpha^7/(15^2\pi^5))^{1/4} \).

The domain of the radial variable \( r \) belonging to the valence region is defined by \( D_{\text{bond}} = [r_c, 2r_a] \) where \( r_c = 1/Z \) is the radius of the nuclear
7.3. Bonding regions

cusp. We have set different error bounds $\delta_{\text{bond}}$ for the atoms with $Z = 1, \ldots, 9, 11, \ldots, 17$. The bulk of the wave functions belong to $D_{\text{bond}}$ with the characteristic amplitude $\max_{r \in D_{\text{bond}}} |\Psi(r)|$. An appropriate error bound for a given valence orbital can be $\delta_{\text{bond}} = 0.01 \max_{r \in D_{\text{bond}}} |\Psi(r)|$ leading to $2 \times 10^{-4} \leq \delta_{\text{bond}} \leq 1.1 \times 10^{-2}$.

According to Sec. 1.5, approximately constant and linear parts of functions are extremely well reproduced in low resolution levels of the MRA expansion and more details are included only at those parts, where the curvature of the function is large. Plotting the radial wave functions defined by (7.7) we could recognize some characteristics of the curves and draw conclusions about the expected features of their MRA expansion. For polarization functions of atoms Li to Cl the exponent ranges between the values 0.175 and 0.8, the most detailed ones are for the largest exponent 0.8 (C, N, O, F), and the most wavelets are needed for those functions. The p-type polarization function exponents of the H and He atoms are 1.1 and 0.75, which have been treated separately. The least favorable shape of uncontracted s and p functions corresponds to the largest exponent in the interval $2.6 \times 10^{-2}$ to $3.6 \times 10^{-1}$ for the elements Li to Cl. The contracted s and p-type valance shell AOs have the most detailed shape in case of fluorine, and the reproduction of this atom’s contracted orbitals needs the most wavelets and the highest refinement levels.

I have expanded the valance shell atomic orbitals and polarization functions to the required precision and counted the total number of necessary wavelets in the MRA representation. The result is shown as a function of the atomic number in Fig. 7.1. The contracted orbitals are the hardest to represent, nevertheless, except for fluorine not more than 25 wavelet functions can sufficiently reproduce valance shell AOs. Polarization and uncontracted functions need considerably less MRA basis functions. The highest necessary resolution level for contracted AOs is $m = 4$, with grid

![Figure 7.1: The number of wavelets required to represent the valance shell atomic orbitals and polarization functions as a function of the atomic number.](image-url)
distance $2^{-4}$ a.u., except for the 2s orbital of fluorine with $m = 5$, while for uncontracted functions the level $m = 1$ is usually sufficient (for N, O and F, $m = 2$ is necessary). For expanding polarization functions the resolution level $m = 2$ or 3 is appropriate.

### 7.4 Nuclear cusps

We have chosen the model radial density function around the nucleus of various atoms in the form $\rho(r) = \rho_0 \exp(-\lambda r)$. The parameter $\lambda$ was set according to the requirement that the density should satisfy the nuclear cusp condition for neutral atoms with nuclear charge $Z$, i.e., $\lambda = 2Z$. As the cusp consists of the electrons of the core 1s orbitals, the normalization factor $\rho_0$ is determined by the condition $\int 4\pi r^2 \rho = 2$, because the cusp is mostly owed to the 1s electrons, thus for atoms above Hydrogen, $\rho_0 = 2Z^3/\pi$.

As before, we have expanded the 1D radial cut of the root of the density with domain $D_{\text{cusp}} = [0, r_c)$. The radius of the cusp was defined previously as $r_c = 1/Z$. Since the essential part of the cusp is at the position $r = 0$, I have artificially extend the function $\sqrt{\rho}(r)$, $r \in [0, \infty)$ by reflecting it to the origin, thus the domain is changed to $D_{\text{cusp}} = (-r_c, r_c)$. Later the number of necessary wavelets was divided by 2.

Although this oversimplified density model does not reflect the real shell structure of atoms [93, 94], the most critical details are compressed in the singularity at the nuclear cusp. As the error of reproduction of the density is the largest at the nuclear positions, and the value of $\rho(0)$ is physically relevant in the isomer shift calculations, based on my supervisor’s idea, we have required that the approximation error of $\rho(0)$ should be less than the change in the density due to electron configuration changes. The permissible error for $\rho$ was taken from previous isomer shift calculations [95] as $0.001\rho(0)$, leading to the error bound $\delta_{\text{cusp}} = 0.0005\sqrt{\rho}(0)$ of $\sqrt{\rho}$. Beside the calculations by requiring the uniform convergence error criterion (7.3), I have also applied a different approach for measuring the approximation error of MRA. Since the value of the density in the cusp region changes by orders of magnitude (especially for large $Z$), one might suspect, that the threshold $\delta_{\text{cusp}}$ is too large around $r \approx r_c$. Alternatively, I have also tested the convergence of the expansion by requiring the relative error condition

$$\left|\sqrt{\rho}^{[m]}(r) - \sqrt{\rho}(r)\right| \leq 0.0005\sqrt{\rho}(r). \tag{7.8}$$

In practice, I have checked the validity of expression $\max_{r \in I_{mk}} |\sqrt{\rho}^{[m]}(r) - \sqrt{\rho}(r)| < 0.0005\max_{r \in I_{mk}} \sqrt{\rho}(r)$, where the grid interval $I_{mk}$ is defined in Sec. 7.1.

Applying any of the above convergence conditions leads to a surprising consequence, which is based on my numerical observation. Following my supervisor’s train of thought, the function we are expanding is written
7.4. Nuclear cusps

as $\sqrt{\rho}(r) = \sqrt{\frac{2}{\pi}} Z^{3/2} \exp(-Z|r|)$ for various atomic numbers $Z$. For the atomic number $\bar{Z} = 2^n Z$ one scales the space variable as $\bar{r} = 2^n r$, leading to $\sqrt{\rho}(\bar{r}) = \sqrt{\frac{2}{\pi}} Z^{3/2} \exp(-\bar{Z} |\bar{r}|) = 2^{3n/2} \sqrt{\rho}(\bar{r})$. As the threshold of acceptable errors scales also by the factor $2^{3n/2}$, it is easily seen, that the MRA expansion of $\sqrt{\rho}(r)$ at the resolution level $m$ and that of $\sqrt{\rho}(\bar{r})$ at resolution level $m + n$ can be transformed to each other by simply multiplying the expansion coefficients with the factor $2^{3n/2}$, thus both satisfies the corresponding error criterion at the same time. The consequence of this fact, that for any $m$ the number of necessary wavelets in the expansion of $\sqrt{\rho}(r)$ and $\sqrt{\rho}(\bar{r})$ coincides at resolution levels $m$ and $m + n$, respectively. We have observed, that due to the above similarity considerations, the total number of wavelets $N_w(Z)$ in a proper expansion behaves as $N_w(Z) = C + 2 \log_2 Z$ for $Z = k2^n$, where the constant $C$ depends on the integer $k$ and on the required error bound.

Fig. 7.2 shows the graphical illustration of the MRA expansion of the density of an ‘oxygen atom’ at consecutive resolution levels. The error of the approximations seems to scale as $\sim 2^{-m}$. The deviation of the approximated function from its approximation at level $m = 6$ is below the required error bound for $|r| \geq 2^{-6} \approx 0.016$. The next refinement step is therefore carried out only in the range $-2^{-6} \leq r \leq 2^{-6}$. The resulting deviation is seen in the right bottom part of Fig. 7.2. As the length of the interval with large error is constant until a given resolution (in this case until $m = 6$), but thereafter decreases rapidly, the feared exponential explosion of the number of necessary wavelets does not happen. For the special values $Z = k2^n$ the increase of $N_w(Z)$ is logarithmic and for arbitrary atomic numbers I have summarized the results of my numerical calculations in Fig. 7.3 both for the absolute and relative error conditions (7.3) and (7.8).

As we see, the overall behavior of $N_w(Z)$ remains roughly logarithmic for arbitrary values of $Z$. In consequence of this logarithmic behavior the demanded resolution does not increase over a manageable level even for large atomic charge and the total number of wavelets for the atoms of the first three rows of the periodic table remains below 35 and 46 for the absolute and relative error criteria, respectively. Using the logarithmic extrapolation, we can conclude, that according to Fig. 7.3 the corresponding number should be in the range 37 to 52, for $Z = 100$.

7.4.1 Derivative singularity

In Fig. 7.2 we can recognize, that zooming onto the cusp region, the exponential decay of the density is very close to the function $\sqrt{\rho}(0)(1 - Z|r|)$, and the linear parts of it are extremely well reproduced by the wavelet expansion. The excellent approximation can be attributed to the previously noted fact (Sec. 1.5), that the Daubechies-4 basis has vanishing first moment, thus it is able to expand linear functions exactly, already at the level
Figure 7.2: Approximations of the electron density around the nuclear cusp of the oxygen atom at maximum resolution levels \( m = 5, 7 \) and 9, respectively. Dotted line shows the exponential form \( \sqrt{\rho(r)} = \sqrt{\rho(0)} \exp(-Z|r|) \), with \( Z = 8 \), and the solid line corresponds to the expansion (5.35). The right hand column shows the deviation of the ideal \( \sqrt{\rho(r)} \) from its MRA approximation. Atomic units are used.

The error is concentrated to those wavelets only, whose support contains the position of the cusp, i.e., the singularity where the shape of the density deviates from linear. Correspondingly, the number of necessary wavelets at these resolution levels is not more than 2 (for cusps centered on non-gridpoints 3), and the total number of these additional basis functions is determined by the decay of the deviation. As we see in the right hand column of Fig. 7.2, the magnitude of the error decreases exponentially with increasing \( m \), and within few local refinement steps at the nucleus reaches the required error bound. According to my calculations the correct description of the cusp singularity requires 4 to 6 wavelets located at the position of...
7.5. Extension to three dimensions

Finally, we have considered the transition from one-dimensional radial cuts of the density to the three-dimensional expansion. A naive approach is simply taking \( N^3_w \) as the approximate number of required wavelets in a 3D expansion of nuclear cusps, which leads to \( \approx 43000 \) if \( N_w = 35 \). This argumentation is, however misleading, as these basis functions belong to different resolution levels in different parts of the 3D space. In order to estimate the number of necessary basis functions in three dimensions, we return in this section to the equivalent basis set containing only scaling functions at the finest resolution level. From the considerations in section 1.4 follows, that the number of necessary scaling functions in a given part of the space is twice the number of the finest wavelets belonging to the same resolution \( m \). This number will be denoted by \( N_m \), and it is known from my numerical studies. The grid length of an arbitrary resolution \( m \) is \( d_m = 2^{-m}d_0 \). The part of the 3D domain \( D_{\text{cusp}} \) which needs a resolution at least \( m \) is a sphere of radius \( N_md_m \), and that part of the domain which needs exactly the resolution \( m \) is the shell outside of the smaller sphere with radius \( N_{m+1}d_{m+1} \). Consequently, the number of grid points where exactly resolution level \( m \) scaling functions are used in the MRA expansion is the volume of the shell compared to the volume of the grid cell, \( \left(4\pi/3\right) \left( N^3_m d^3_m - N^3_{m+1}d^3_{m+1} \right)/d^3_m \).
From the previous calculations it also turns out, which is the minimum level of resolution $m_{\text{min}}$ describing the farthest parts of the 3D domain $D_{\text{cusp}}$ sufficiently and the maximum $m_{\text{max}}$ at the position of the nucleus. The number of scaling functions required in a 3D MRA calculation is finally determined by

$$N_w = (4\pi/3) \sum_{m=m_{\text{min}}}^{m_{\text{max}}} (N_m^3 - N_{m+1}^3)/8.$$ (7.9)

Using the 1D values belonging to the absolute error criterion one estimates the number of necessary basis functions in 3D expansions in the range 1400 to 3400, which is much less then the naive estimation.

![Figure 7.4: The deviation of the ideal $\sqrt{\rho}(r) = \sqrt{\rho}(0) \exp(-Z|r|)$ from its MRA approximation according to (5.35) in one and two dimensions at resolution levels $m = 5$ and 6. Atomic units are used.](image)

After modifying the algorithm for two and three dimensions, it turned out, that the necessary resolution level increases by 1 and 2 compared to the 1D results for the 2D and 3D cases, respectively. The reason of this phenomenon is that the effective relative error is the sum of the relative errors of the original functions, if the functions are multiplied. The maximum of the function is the same for all the dimensions (they are chosen to be the one and two dimensional cuts of the 3D $\sqrt{\rho}$), thus the deviation of the approximating and approximated functions gets larger as the dimension grows. This fact is also demonstrated in Fig. 7.4, where the error of the $m = 5$ and 6 approximation is plotted for the $Z = 8$ oxygen atom in one
and two dimensions. The 2D plot is not a cut, the surface is rotated in a manner, that one of the coordinates is orthogonal to the paper. The increment does not belong to the derivative singularity region, unfortunately, causing much larger number of necessary wavelets, than we have expected.

I have computed the number of necessary wavelets in two and three dimensions for \( Z = 2^n \), for both the relative and absolute error criteria. A scaling rule similar to the 1D case can be found. As the atomic number doubles, the required resolution level grows by 1 and the number of necessary wavelets increases by \( 2^D \), resulting in the numerical fit

\[
N_w(Z) = 852 + 4 \log_2 Z \quad (7.10)
\]

\[
N_w(Z) = 1485 + 4 \log_2 Z \quad (7.11)
\]

for the 2D case, and

\[
N_w(Z) = 21289 + 8 \log_2 Z \quad (7.12)
\]

\[
N_w(Z) = 57093 + 8 \log_2 Z \quad (7.13)
\]

for 3 dimensions. The upper equations (Eq. 7.10 and 7.12) belong to the absolute error criterion, and the other two to the relative one.
CHAPTER 7. ADAPTIVE REFINEMENT OF THE...
Chapter 8

Two-electron density matrices

8.1 Representation of the Kato electron electron cusp condition

Multiresolution analysis expansion (5.22) of the spin traced two particle density matrix can be substituted into the Bingel formula (3.11). The spherical average of the diagonal expanding functions \( \vartheta^{A,m}(r_1, r_2| r_1, r_2) \) and \( \vartheta^{B,m}(r_1, r_2| r_1, r_2) \) was taken after transformation the variables to \( R \) and \( u \), similarly to the step (3.2), resulting in the expanding functions \( \vartheta^{A,m}(R, u) \) and \( \vartheta^{B,m}(R, u) \). The correlation cusp condition turned then into

\[
\sum_{k_1 k_2} \left[ g^{A,m}_{k_1 k_2 \ell_1 \ell_2} \vartheta^{A,m}_{k_1 k_2 \ell_1 \ell_2}(R, u) + g^{B,m}_{k_1 k_2 \ell_1 \ell_2} \vartheta^{B,m}_{k_1 k_2 \ell_1 \ell_2}(R, u) \right] \approx (1 + u) \sum_{k_1 k_2} \left[ g^{A,m}_{k_1 k_2 \ell_1 \ell_2} \vartheta^{A,m}_{k_1 k_2 \ell_1 \ell_2}(R, 0) + g^{B,m}_{k_1 k_2 \ell_1 \ell_2} \vartheta^{B,m}_{k_1 k_2 \ell_1 \ell_2}(R, 0) \right].
\]

(8.1)

If real valued wavelets and scaling functions are used, which is quite common, the new expanding functions of type \( B \) are \( \vartheta^{B,m}_{k_1 k_2 \ell_1 \ell_2}(R, u) = 0 \). In the next sections the real valued MRA basis set of Alfred Haar is used.

8.2 Reproduction of the cusp condition in one dimension using Haar basis set

The spherical average for a function \( f(u) \) in case of one dimensional variable \( u = u \) is simply

\[
\overline{f}(u) = \frac{f(u) + f(-u)}{2} = \frac{f(u) + f(-u)}{2}. \tag{8.2}
\]
This results in really easy averaging of the expanding functions $\vartheta^{A,m}$ and $\vartheta^{B,m}$ in the one dimensional space, especially if the symmetry properties of the density matrices (2.10) are used, leading to

$$
\overline{\vartheta}^{A,B,m}_{k_1 k_2 \ell_1 \ell_2}(R,u) = \vartheta^{A,B,m}_{k_1 k_2 \ell_1 \ell_2} \left( R + \frac{u}{2}, R - \frac{u}{2} \right) . \quad (8.3)
$$

Multiresolution analysis offers a natural, infinitely dense lattice, thus it is enough to ensure the satisfaction of the condition (8.1) in these points. Since the grid points are equivalent, choosing $R$ to be 0, does not restrict the generality of the study. Introducing the notation $v = \frac{1}{2} |u|$, and using the fact, that Haar basis functions are real, results in

$$
\vartheta^{A,m}_{k_1 k_2 \ell_1 \ell_2}(0,u) = \vartheta^{A,m}_{k_1 k_2 \ell_1 \ell_2}(v,v) \approx (1 + 2 |v|) \sum_{k_1 k_2 \ell_1 \ell_2} g^{A,m}_{k_1 k_2 \ell_1 \ell_2} \vartheta^{A,m}_{k_1 k_2 \ell_1 \ell_2}(0,0,0) . \quad (8.4)
$$

First, the problem was solved at a given resolution level $m$, in purely scaling function basis. In this case

$$
|u|^m = \sum_\ell h_{m \ell} s_\ell(u), \quad (5.23)
$$

where

$$
h_{m \ell} = \left< s_\ell(u) \right| |u| \left>= \int |u| s_\ell(u) \, du = 2^{-3m/2} |\ell + \frac{1}{2}| . \quad (8.5)
$$

Here, $(2^{-m}) |\ell + \frac{1}{2}|$ is the distance of the center of the scaling function $s_\ell$ from the origin, i.e., the value of $|u|$ in the center of $s_\ell$, while $2^{m/2}$ is the value of this basis function in the same place. If $v \in [2^{-m} \ell, 2^{-m}(\ell + 1))$, then

$$
s_{m \ell}(v) = 2^{-m/2} \delta_{\ell,v} \quad \text{and} \quad s_{m \ell}(-v) = 2^{-m/2} \delta_{-\ell-1,-\ell'}. \quad (8.6)
$$

Substituting these values into (5.23), the l.h.s of Eq. (8.4) turns into

$$
2^{-m/2} \left( g^{A,m}_{\ell,-\ell-1,\ell,-\ell-1} + g^{A,m}_{-\ell-1,\ell,-\ell-1,\ell} \right) = 2 \cdot (2^{-2m}) g^{A,m}_{\ell,-\ell-1,\ell,-\ell-1} . \quad (8.7)
$$

where the symmetry property (5.30) was used. Similar considerations together with the expansion (8.6) of function $|u|$ led to the following form of the cusp condition

$$
g^{A,m}_{\ell,-\ell-1,\ell,-\ell-1} \approx (1 + 2 |\ell + \frac{1}{2}| \cdot 2^{-m}) g^{A,m}_{0000} . \quad (8.8)
$$
8.3 Numerical reproduction of the electron-electron cusp

Worth to mention, that the spherically averaged correlation cusp condition (3.11) does not provide information about all the coefficients $g_{\ell_1\ell_2k_1k_2}^{A,m}$ with any index combinations.

Similar but more complex calculations can be executed for the more general form of the Bingel condition (3.8), with the choice $R = (2^{-m})L$ and $R' = (2^{-m})K$, and the new variables $|u|/2 = v \in (2^{-m}\ell, 2^{-m}(\ell + 1))$ and $|u'|/2 = v' \in (2^{-m}k, 2^{-m}(k + 1))$. Substituting the $m$th level scaling functions into definitions (5.23) and (5.24), and using the index symmetries (5.30), the cusp condition turns into an equation of the expansion coefficients

$$g_{L+\ell,L-\ell-1;K+k,K-k-1}^{A,B,m} \approx \left(1 + (|\ell + \frac{1}{2}| + |k + \frac{1}{2}|) \cdot 2^{-m}\right) g_{L,L,K,K}^{A,B,m}. \quad (8.10)$$

This approximation is true for the expanding functions $\vartheta^A$ and $\vartheta^B$ separately, resulting in two independent electron-electron cusp conditions, for the coefficients of type $A$ and $B$. Although, approximation (8.10) is only valid for even index differences $\ell_1 - \ell_2$ and $k_1 - k_2$, I suggested to generalize it for any index-quartets $\ell_1, \ell_2, k_1, k_2$ as

$$g_{\ell_1\ell_2k_1k_2}^{A,B,m} \approx \left(1 + \frac{1}{2}(|\ell_1 - \ell_2| + |k_1 - k_2|) \cdot 2^{-m}\right) g_{L,L,K,K}^{A,B,m}. \quad (8.11)$$

Here, the notation $L = [(\ell_1 + \ell_2 + 1)/2]$ and $K = [(k_1 + k_2 + 1)/2]$ was introduced, with $\lfloor x \rfloor$ meaning the floor of $x$.

Approximation (8.11) describes the singular behaviour of coefficients $g^A$ and $g^B$, but according to (3.8) some other terms, linear functions of the index differences $(\ell_1 - \ell_2)$ and $(k_1 - k_2)$ can also appear. The cusp condition itself does not provide any information about the coefficients $g_{L,L,K,K}^{A,m}$ and $g_{L,L,K,K}^{B,m}$; we can only know, that they are some smooth functions of the indices $K$ and $L$. Generally, these coefficients could be used for energy minimization, with the constraint, that the diagonal elements of type $g_{L,L,L,L}^{A,m}$ are strongly connected to the electron density and $g_{L,L,L,L}^{B,m} = 0$, according to its symmetry properties (5.30).

8.3 Numerical reproduction of the electron-electron cusp

I have performed numerical calculations using Haar scaling functions in the MRA expansion (5.22) of the two-particle density matrix with the coefficients (8.11) in order to demonstrate our results. The correlation cusp condition is valid only in a narrow environment of the $u = 0$ points, thus an exponential decrease was given to the coefficients in a manner, that around $u = u' = 0$ the value and the slope of the function should not change, and the maximum value of the function should be at about 1 a.u distance from the cusp. In Fig. 8.1 the cut of the two electron density matrix $\gamma^A_2$ at
CHAPTER 8. TWO-ELECTRON DENSITY MATRICES

Figure 8.1: The two-particle density matrix $\gamma^2$ as function of coordinates $u$ and $u'$, with the constraint $R = R' = 0$, at resolution levels $m = 4$ and $m = 5$.

Figure 8.2: The $u' = u$ cut of the two-electron density matrix as a function of the electron separation $u$, with the constraint $R = R' = 0$, at resolution levels $m = 4$ and $m = 5$.

$R = R' = 0$, as a function of the difference coordinates $u$ and $u'$, at resolution levels $m = 4$ and $5$. The $1 + |u|/2 + |u'|/2$-type character of the cusp is clearly observable, the tulip-like shape is caused by the exponential cutoff.

The $u = u'$ cut of Fig. 8.1 is shown on the next plot, in Fig. 8.2. In Fig. 8.3 the ratio of the approximated $1 + |u|$ cusp and its approximation is also plotted, of course, no exponential cutoff was given to the function. It can be seen, that the relative error scales as $2^{-m}$.

The programs offer the possibility to replace the center coordinates $R$ and/or $R'$ from the origin. Fig. 8.4 shows the two dimensional cut of the $m = 4$ level expansion of the density matrix with one of the center coordinates remaining zero, but the other moved to an $m = 5$ grid point and to a non-grid point. The 1D $u = u'$ cuts of the plots in Fig. 8.4 are shown in Fig. 8.5. The results, compared to the first plot of Fig. 8.2, which is in the same resolution level, show, that in these cases the shape of the approximation deviates less from the original function, than it does in the $R' = 0$ case.
8.3. Numerical reproduction of the electron-electron cusp

Figure 8.3: Two-electron density matrix as a function of the electron separation \( u = u' \), with the constraint \( R = R' = 0 \), at resolution levels \( m = 4 \), \( m = 5 \) and \( m = 6 \). The ratio of these functions to the original \( 1 + |u| \) is also plotted.

Figure 8.4: The two-particle density matrix \( \gamma_s^2 \) as function of coordinates \( u \) and \( u' \), at resolution level \( m = 4 \). The center coordinates are chosen to be \( R = 0, R' = 1/32 \) at the first plot and \( R = 0, R' = 0.023 \) at the second.

Figure 8.5: Two-electron density matrix as a function of the electron separation \( u = u' \), at resolution level \( m = 4 \), with the constraint \( R = 0 \) and \( R' = 1/32 \) in the first plot and \( R' = 0.023 \) in the second. The ratio of the approximation and the approximated function is also plotted.
8.4 Transition between the fine and the rough refinement levels using Kato’s electron-electron cusp condition

In this section, we still remain at the Haar basis set. After getting more familiar with the pyramid algorithm, I have revised the first variant of this result, which appeared in [90]. Changing the resolution level from fine to a rougher one is a unitary transformation consisting of (1.1) and (1.4), which has inverse, Eq. (1.5). Let us take one refinement step, for simplicity, from m = 0 to m = 1. Using the matrices L and H of the Pyramid algorithm (1.12), it is possible to derive the rough wavelet and scaling function coefficients from the finer resolution scaling function coefficients of the MRA expanded two-electron density matrix as

\[ g_{11,11,12}^{A,B,0} = \frac{1}{4} \sum_{\lambda_1=0,1} \sum_{\lambda_2=0,1} g_{11,11,12}^{A,B,1} \]  

(8.12)

Substituting the cusp conform expression (8.11) for \( m = 1 \) into the right hand side of (8.12) we arrive at terms containing \( g_{LL'K'K'}^{A,B,1} \) where \( L' \) is restricted to \( \ell_1 + \ell_2 \) or \( \ell_1 + \ell_2 + 1 \) and a similar constraint is true for \( K' \). According to the idea of my supervisor, the smooth dependence on indices can be expressed as \( g_{LL'K'K'} \approx g_0 + (L' - K') \Delta g + \ldots \) which results in the first order

\[ g_{LL'K'K'}^{A,B,1} \approx g_{LL'K'K'}^{A,B,1} + \Delta g^{A,B}, \]

\[ g_{LL'K'K'}^{A,B,1} \approx g_{LL'K'K'}^{A,B,1} - \Delta g^{A,B}, \]

\[ g_{LL'K'K'}^{A,B,1} \approx g_{LL'K'K'}^{A,B,1}. \]  

(8.13)

Using these approximations in (8.12) it can be realized that a relation similar to (8.11) holds for almost all index combinations \( \ell_1, \ell_2, k_1, k_2 \) of the first level expansion coefficients, supposing that the following scaling transformation equation is valid for the fine—coarse transition

\[ g_{LLKK}^{A,B,0} = 4 \cdot g_{LL2L2K}^{A,B,1}. \]  

(8.14)

This result indicates that the local form of the correlation cusp condition (3.11) is satisfied in a scale invariant way by (8.11) and (8.14).

The opposite, coarse—fine, transformation is trivial for even index values, however, continuity on indices implies a linear interpolation formula for odd labels

\[ g_{2L+1 2L+1 2K 2K}^{A,B,1} = \frac{1}{2} \left( g_{2L 2L 2K 2K}^{A,B,1} + g_{2L+2 2L+2 2K 2K}^{A,B,1} \right), \]  

(8.15)

\[ g_{2L 2L 2K+2 2K+2}^{A,B,1} = \frac{1}{2} \left( g_{2L 2L 2K 2K}^{A,B,1} + g_{2L 2L 2K+2 2K+2}^{A,B,1} \right), \]  

(8.16)

\[ g_{2L+1 2L+1 2K+1 2K+1}^{A,B,1} = \frac{1}{2} \left( g_{2L 2L 2K 2K}^{A,B,1} + g_{2L+2 2L+2 2K+2 2K+2}^{A,B,1} \right). \]  

(8.17)
8.4. Transition between the fine and the rough refinement levels...

By applying the cusp condition (8.11), the off-diagonal finer resolution level expansion coefficients can also be calculated. Knowing the scaling function expansion coefficients (8.14)–(8.17) the wavelet coefficients can be calculated using the Pyramid algorithm (1.12), and it can be seen, that condition similar to (8.11) holds also for the wavelet coefficients of the same resolution level. For mixed refinement level wavelet coefficients the scaling of the cusp is not trivial.

The above considerations are also applicable for the transitions between arbitrary resolution levels $m$ and $m+1$ leading to the scaling transformation (8.14) for $g_{A,B,m}^{LLK}$ and $g_{A,B,m+1}^{2L2L2K}$.
Summary

In the present dissertation first I have summarized the necessary aspects of multiresolution analysis. The basis functions of MRA, the wavelets and scaling functions decompose the Hilbert space of squarely integrable functions into resolution levels, and own the following advantageous properties. They can be chosen in such a manner, that they are orthonormal, compactly supported, differentiable, and generated by simple translations and dilations from one common function. The refinement of the not sufficiently fine resolution can be naturally performed by introducing wavelets of the next level, without loosing the coarser expansion, which has been already elaborated. The expansion coefficients are connected to each other by the pyramid algorithm (1.1), (1.4) and (1.5).

Slater determinants built from these basis functions are capable to approximate \( N \)-electron wave functions as (5.4), and the density operators can be expanded with real expansion coefficients by the Hermitic operators of type \( \hat{A} \) (5.8), \( \hat{B} \) (5.8) and \( \hat{P} \) (5.6). Reduction of degrees of freedom does not change the type of the basis functions, only the properties of the expansion coefficients. After spin tracing we have expanded the kinetic (4.10) and the electron-electron interaction (4.11) energy, and we could have concluded, that their calculation can be reduced to determination of a limited number of integrals, which are universal in the sense, that they depend only on the type of wavelets, and are independent of the system properties. Due to the compact support of wavelets, these integrals are mostly zero, thus they are very easy to handle and store. This finding, together with the fact that very high and low resolution terms are negligible, can lead to an efficient representation of density operators and energy density functionals.

We have developed a method for determining the expansion coefficients of the electron density and, by using density data only, the one-particle density matrix. In the simplest case the resulting density operator describes a Bose condensate, however, by a proper modification, the method yielded an \( N \)-representable fermionic one-particle density operator in the fine resolution limit, and at the same time an excellent quality density function even at low resolutions.

We have compared the results of our method to the Macke-Harriman construction based on delocalized Fourier-type orbitals. It turned out, that
the localized nature of the scaling functions describes the details of the electron density better, than the delocalized representation. This observation is similar to the fact found earlier in the field of compression and storage of picture and sound, that made the wavelet based description preferable to the Fourier expansion methods.

Due to the localized representation we were able to include electron correlation in the sense that the constructed density operator goes beyond the restricted Hartree-Fock level.

We have also shown that the deviation of the exact kinetic energy term from the Weizsäcker expression is not a necessary consequence of the Pauli-principle, since by a direct construction we have found a density operator which is correlated, \( N \)-representable in the fine resolution limit, although it results in the Weizsäcker kinetic energy term.

Studying the MRA expansion of the electron density in various molecular regions, we arrived at the quite surprising result that a scaling function basis set sitting on a rather coarse grid of grid length \( d_0 = 0.5 \) a.u. is capable of describing the density with an acceptable precision in most parts of the molecules, except for the bonding and nuclear cusp regions. Thus, it is inferred that the zero level approximation of a realistic calculation should be chosen by the scaling function MRA basis set separated by the distance \( d_0 = 0.5 \) a.u., and further refinements by introducing wavelet basis functions are necessary only at chemical bonds and around the nuclei.

We have shown that the number of required wavelet basis functions is finite in both the bonding and cusp regions. The amount of necessary wavelets in the cusp at nucleus \( a \) increases with the logarithm of the atomic number \( Z_a \), and its moderate growth remains manageable for extremely heavy atoms, as well. Supposing, that the system contains only first to third row atoms, the description of the nuclear cusp regions of the whole molecule does not require more than \( 35N \) wavelet basis functions, if \( N \) is the number of atoms in the studied system. This estimation can be considerably better for molecules containing mainly light atoms. As we have emphasized previously, the bonding regions are well described by less than 25 wavelets as a rule, leading to an increment of \( 25N \sim N \) basis functions.

These values have been determined using illustrative calculations by the Daubechies-4 wavelet basis set. Going to more sophisticated wavelets (like Daubechies-6 or higher) which provide higher vanishing moments, we expect that those parts of the density or wave function, where the curvature is large can be reproduced more easily at lower resolution levels, decreasing in this way the total number of basis functions achieved by applying Daubechies-4.

The expectation values of one particle operators are calculated using their trace with the one particle density matrix. In chapter 7 the required the number of wavelets for reproducing the density is studied, and it turned out, that it is proportional to \( \log_2 N \). Considering the fact found in chapter 6, that an expansion coefficient matrix of the one-electron density matrix which
is compatible both with the Pauli principle and the electron correlation should rather have a block diagonal form, thus the number of significant expansion coefficients of the one-particle density matrix scales similarly to those of the density, as \( \sim \log_2 N \). Any expectation value calculated as \( \text{Tr}(\cdot \gamma_i^\dagger) \) only those coefficients \( g_{k\ell A, B, m} \) contribute, where the support of \( w_{mk} \) and \( w_{m\ell} \) overlap. For the Daubechies-4 basis set this requirement leads to \( |k - \ell| \leq 2 \).

In three dimensions the number of necessary basis functions is considerably larger, but scales similarly to the 1D case. This emphasizes the need for very simple and effective algorithms for calculating one- and two-electron integrals.

The Kato electron-electron cusp condition can be fulfilled by Eq. (8.1) for the expansion coefficients. For Haar wavelets, this equation is very simple, and it has been adapted for numerical calculations. From a finer resolution level it is natural to obtain a rougher one by application of (8.14), which is based on the pyramid algorithm. However, it is also possible to define inverse of this transformation, which can be interpreted as a kind of inverse renormalization.
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