

# Wavelet Based Density Matrices, Electron Density and Energy Functionals

Summary of the PhD Thesis

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# 1 Introduction

Multiresolution analysis (MRA) or wavelet analysis is a rapidly developing field of applied mathematics, which can treat the square integrable functions at different resolution levels, and, adapted to the shape of the function, it is able to use various resolution levels. Two types of basis functions are applied in MRA, scaling functions span the resolution levels, and wavelets ensure the link between the levels, i.e., the local refinement. Both types of basis functions can be generated in a similar way. They are originated from a mother function by translation on an integer grid and then dilation. Both can be chosen compactly supported and differentiable at the same time. (A function is called compactly supported, if its value is zero outside of an interval, outside of its support.) The possibility of local refinement, the compact support and the similar shape of the basis functions can lead to largely simplified electron structure calculating methods, since the great demand of computing capacity of these algorithms can be attributed to either the complicated form or the large number of basis functions they use.

One of the most promising electron structure calculating methods is density functional theory (DFT), and we have chosen to work within its framework. According to the Hohenberg–Kohn theorems [Hohenberg,Kohn,1964], the ground state energy of a system can be written as a functional of its electron density, there exists a one to one mapping between the ground state density and the external potential, and the ground state density minimizes the energy functional. Unfortunately, the shape of the whole system’s energy functional is not known, only the external potential energy part of it. However, by using reduced one- and two-electron density matrices, the kinetic and electron-electron interaction energy can be expressed. The one- and two-electron density matrices arise from the total  $N$ -electron density matrix by tracing all its spin variables, and  $N - 1$  or  $N - 2$  of its spatial coordinates. Such reduction of degrees of freedom is called contraction. The question, whether the reduced density matrices and the density could be originated from a physical  $N$ -electron density matrix is known as  $N$ -representability problem. A one-electron density matrix is  $N$ -representable, if and only if its eigenvalues, i.e., the natural occupation numbers are between 0 and 2. This condition is the generalized Pauli principle [Coleman,1981], and such necessary and sufficient condition of  $N$ -representability does not exist yet for reduced density matrices with higher electron number.

Kato’s cusp conditions [Kato,1957] reflect derivative point singularities of the density and the two-electron density matrix. The nuclear cusp is easily reproducible by Slater-type orbitals within the Hartree-Fock framework while the electron-electron, or correlation cusp condition can be fulfilled by the usual methods very hardly, only by introducing complicated correction factors. We have seen, that by applying scaling functions, this problem can be solved in a very natural way.

## 2 Objectives

During my PhD work I dealt with multiresolution analysis of density matrices, electron density and energy density functionals. After producing the one- and two-electron density matrices, we have studied, what kind of MRA-expansion of the energy functionals they are leading to, and the results rose great expectations.

The energy as the functional of the density can be defined in several ways, and we have chosen Lieb's functional [Lieb,1985], which is based on the density operators. For deriving the Lieb's functional such one- and two-particle density matrices are needed, which lead to a prescribed electron density, thus we have studied, how the MRA-expansion of a given density can be used for deducing the reduced density matrix of an  $N$ -particle bosonic or fermionic system. Since the electron structure has different detail characteristics in different spatial regions, i.e., various resolution levels are needed, the possibility of local refinement, offered by the wavelets, can play an essential role in reducing the number of necessary basis functions for reproducing the density and the density matrices. This fact was both numerically and analytically verified.

We have also analyzed the scaling function based realization of the electron-electron cusp condition, this electron correlation reflecting property of the two-electron density matrix. The studies mentioned above can lead to an own multiresolution analysis based electron structure calculating method and can be used for checking the already existing methods [Arias, 1999].

## 3 New scientific results

### I. *MRA-expansion of the density matrices, the contraction and the energy terms*

Based on symmetry considerations, for expanding the  $N$ -electron density matrices I have introduced three types of functions built from scaling functions. I have verified, that by the reduction of degrees of freedom the different types of functions are not transformed into each other, but to same types of functions with smaller electron number. I have also given the expansion of spin traced reduced one- and two electron density matrices. I have detected, that the kinetic and the electron-electron interaction energy can be written as single or triple sums of overlap and two-electron integral-like terms. Because of the compact support of the scaling functions, most of the terms are zero. The non-zero terms do not depend on the actual system parameters, only on the type of MRA basis functions, thus after calculating them, they can be organized to databases, and it is not necessary to calcu-

late them again for an other system, as in case of integrals of usual atomic basis functions. The coefficients in the sums are the expansion coefficients of the one- and two-electron density matrices. [1]

II. *Scaling function expansion of a prescribed electron density*

For producing the Lieb's functional such density matrices are needed, which result in a prescribed electron density. Objects consisting of two scaling functions' product can be used for expanding a given density. The reason of this strange expansion is that the density does not belong to our Hilbert space, thus multiresolution analysis can not be applied directly to it, while the square root of a density is square integrable, thus it can be expanded by scaling functions and wavelets. The coefficients in the expansion of the density can be derived from products of the coefficients of the scaling function expansion of the root of the density. However, I have observed, that because of the compact support of the scaling functions most of these coefficients belong to trivially zero expanding functions, thus they do not influence the density. [3]

III. *The MRA-based shape of the bosonic one-particle density matrix*

Since the expanding coefficients of the density can be originated from those of the one-particle density matrix, it seems to be natural to originate the expansion coefficients of the matrix to the already known expansion coefficients of the density. However, I have proved, that if the density coefficients arising as products of the MRA-coefficients of the root of the density are applied, the resulting density matrix does not fulfill the generalized Pauli principle, moreover, all of its natural occupation numbers are zero, except for one, which is  $N$ , thus the matrix characterizes a Bose condensate. [3]

IV. *One-particle density matrix describing a correlated electron system*

Since lot of the coefficients in the density's expansion belong to trivially zero expanding function, their value can be chosen arbitrarily. Choosing these coefficients in a proper way can assure that the resulting density matrix fulfills the generalized Pauli principle. If instead of some coefficients arising as the product of two coefficients in the MRA-expansion of the root of the density (i.e., bosonic coefficients) zero is used in the expansion of the one-particle density matrix, the result can be  $N$ -representable. I have set such elements to 0, that the remaining coefficient matrix was block-diagonal, with almost all the block eigenvalues being zero, except for one, which was 1 (or 2, in the spin traced case). I have written back those elements, which were essential in reproducing the density into the block-diagonal coefficient matrix, and proved, that the resulting one particle density matrix, describes a Fermi-system, and approximates the prescribed density correctly in

the fine resolution limit. I have also concluded, that the deviation of the kinetic energy from the von Weizsäcker term can not be ascribed to purely correlation considerations. [3]

V. *Local refinement of the density's approximation in one dimension*

Since different resolution levels can be sufficient for describing different parts of a molecule or a crystal (like the surroundings of the nuclei, the bonding and the asymptotic regions), I have studied, how many wavelets and how many consecutive refinements steps are needed for an approximation of the electron system within proper error bound. The starting resolution level was determined so, that it could reproduce the known asymptotic density with sufficient precision, thus the starting scaling function resolution level was the one with translation constant 0.5 a.u. This expansion can be used for the basis of local refinements by wavelets, where it is necessary.

The hardest task is to reproduce the nuclear cusps, where 10-12 refinements were needed. I have written a program, which gives the approximations of the function at different resolutions, moreover counts the number of essential wavelets at each level. My numerical experiences have shown, that by doubling the atomic number, the number of necessary wavelets of a resolution level is shifted one level up, thus the required resolution grows by one and the total number of used wavelets increases by the length of the cusp region in the units of the starting resolution level. This observation can also be verified by analytic considerations, using the scaling properties of the density, the required precision and the wavelets.

For describing the bonds contracted and uncontracted Gaussian basis functions were applied. In their approximations not more than six refinement steps were needed for the quickly varying contracted orbitals, and 2 to 4 refinements for the uncontracted ones. [4]

VI. *The total number of wavelets used to reproduce the nuclear cusp as a function of the dimension*

I have generalized the algorithm counting the number of necessary wavelets in order to reproduce the density to two and three dimensions. Numerical observations have confirmed the 1D fact, that the number of required wavelets in a resolution level is shifted one level up, if the atomic number doubles. Since the dimension of the interval belonging to the cusp has grown, the increment in the total number of wavelets scales with the  $D$ th power of the one dimensional case, if  $D$  is the dimension. These two experiences can be summarized in the formula for the total wavelet number  $const + 2^D \log_2 Z$ , where  $Z$  means the atomic number. [4]

VII. *Reflection of the electron-electron cusp condition in the coefficients of the two-particle density matrix*

The correlation cusp condition, which can be reproduced very hardly by usual electron calculating methods, is simplified into an equation between the diagonal and the off-diagonal coefficients of the two-electron density matrix in scaling function basis. I have derived a formula for giving the off-diagonal coefficients from the diagonal ones in such a way, that the resulting density matrix reflects the electron-electron cusp condition, without introducing artificial corrections. I have also demonstrated the validity of our formula numerically. [2]

VIII. *Scaling properties of the finer and rougher resolution level expansion coefficients of the two-electron density matrix*

Using the toolkit of multiresolution analysis the rougher resolution scaling function coefficients can be derived from the finer ones, while the transformation to the opposite direction is only possible, if the wavelet expansion is also known. However, I have observed an interesting scaling property of the scaling function coefficients of the two-particle density matrix based on my numerical reproduction of the electron-electron cusp by Haar basis set. I have also given a rule for constructing the finer resolution diagonal coefficients from the rougher diagonal coefficients by using the smoothness of the spatial dependence of the coefficients. Applying the cusp condition formula mentioned in the previous point can provide the finer resolution off-diagonal coefficients, as well. [2]

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## Publications related to the thesis

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- [2] J. Pipek, and Sz. Nagy, *Representation of the Kato Electron-Electron Cusp Condition by Wavelet Based Density Operator Expansions*, Phys. Rev. A **64**, 052506 (2001)
  
- [3] J. Pipek, and Sz. Nagy, *Local expansion of  $N$ -representable one-particle density matrices yielding a prescribed electron density*, J. Chem. Phys. **119**, 8257 (2003)
  
- [4] J. Pipek, and Sz. Nagy, *Adaptive local refinement of the electron density, one-particle density matrices and electron orbitals by hierarchical wavelet decomposition*, under publication at J. Chem. Phys.