Electron Correlation in Orbital Dependent Functionals

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This work presents the latest leg of my path in life. In modern theoretical Physicists’ language I would say that I am looking for the theory of everything. In the more ancient words of Goethe, translated into English by Bayard Taylor\(^1\), I hope

That I may detect the inmost force
Which binds the world, and guides its course.

Unlike Faust I did not make a deal with the devil to accomplish my goals. Rather, I sought help from many people. The help I was granted was not only scientific. I also got help during my everyday life as well as support on my path. This chapter is intended to express my appreciation to all people that guided my course to detect that of the world.

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\(^1\)Gutenberg Project www.gutenberg.net
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That I may detect the inmost force
Which binds the world, and guides its course.

Julia ich liebe dich.

My thoughts go out to Patricia Delameida and her kids. I am sorry for making a promise that I could not keep.

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Introduction

Layout of Introduction
Section 1.1 gives an introduction to Quantum Chemistry. It is intended for the non-expert readers. The Schrödinger Equation is presented as the central equation in Quantum Mechanics. Basic assumptions in Quantum Chemistry are introduced. Achievements and goals of Quantum Chemistry are summarized. Three important methods, Hartree Fock (HF) [1, 2], Density Functional Theory (DFT) [3, 4] and Density Matrix Functional Theory (DMFT) [5, 6], are introduced. The important concept of correlation is explained.

Section 1.2 provides the introduction to Part I: Orbital Dependent Functionals (ODF) in Density Functional Theory (DFT). The main steps in development of DFT are given. Shortcomings of present functionals are mentioned. Orbital Dependent Functionals (ODF) are motivated as a remedy. Three types of ODF are introduced. Difficulties associated with calculating the solution of ODFs are described. The Optimized Effective Potential Method (OEP) is introduced as a solution. Problems and solutions to solve the OEP equations are discussed. Finally, the results of Chapters 3, 4 and 5 are summarized.
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Section 1.3 gives the introduction to Part II: Orbital Dependent Functionals (ODF) in Density Matrix Functional Theory (DMFT). The available classes of ODF in DMFT are introduced. The downside of the most successful functional is explained. The results of Chapter 8 are summarized.

Both, Density Functional Theory and Density Matrix Functional Theory, are approximations to the Schrödinger Equation. Section 1.4 presents the non-relativistic Schrödinger Equation. Its electronic equivalent in the Born-Oppenheimer approximation is derived. In Section 1.5 density matrices are introduced. The important quantities electron density and one-electron reduced density matrix of Parts I and II, respectively, are defined. Finally, in Section 1.6 correlation energy is defined for Hartree Fock (HF), Density Functional Theory (DFT) and Density Matrix Functional Theory (DMFT).

1.1 Introduction to Quantum Chemistry

What does science do?
Science sets out to describe the world only with logic and rationing and leave out any supernatural explanations. From the beginning, scientists tried to explain natural phenomena by basic behavior of smaller parts. Starting with Aristotle, who used his elements - water, fire, earth, air and aether - to describe the world, the known world was divided in ever smaller parts. By doing so scientists hoped to find simple and globally applicable relations between the small parts of nature.
1.1. INTRODUCTION TO QUANTUM CHEMISTRY

Celestial Mechanics
With the invention of celestial mechanics by Sir Isaac Newton in 1687 it was possible to describe all interaction between matter based on gravity. At the end of the 19th century it was believed that the whole world could be described with the Newtonian Equations of motion. The feeling was that there are only particularities to solve but the underlying theory shouldn’t be changed anymore.

Quantum Mechanics
In 1900, however, Max Planck introduced a new theory: Quantum Mechanics. The new theory was driven by experiments which couldn’t be explained by celestial mechanics. Quantum Mechanics describes the behavior of particles at the molecular and submolecular scale. The major innovation of the theory is the duality of particles and waves. Any type of matter should be described not as a mass dot - as is the case in celestial mechanics - but as a wave. The central equation is the famous Schrödinger Equation.

The Schrödinger Equation
The Schrödinger Equation describes the behavior of all matter in the non-relativistic limit. The solution will result in a complete knowledge of the system under consideration. Unfortunately, even for medium sized systems, it is impossible to solve the Schrödinger Equation exactly. Hence, a large effort is spent to find approximations.

What does Quantum Chemistry do?
Quantum Chemistry deals with the formulation, assessment and application of approximate solutions of the Schrödinger Equation. The systems under consideration are of the size of molecules. At this scale three basic assumptions are useful.

1. It is noted that the mass of the nuclei exceeds the electron
mass by far. This leads to the Born-Oppenheimer approximation, which treats the nuclei as charged dots, whereas the electrons are treated quantum mechanically.

2. Time is separated. Most questions in Quantum Chemistry address only static properties. Consequently, space and time coordinates are separated.

3. Relativistic effects are neglected.

This work only deals with non-relativistic time-independent electronic structure theories. The underlying electronic Schrödinger Equation (1.1) will be presented in Section 1.4.

\[
\hat{H}\psi(x_1, \ldots, x_N) = E\psi(x_1, \ldots, x_N) \tag{1.1}
\]

Where \( E \) is the energy and \( \hat{H} \) is called the Hamilton operator. The wave function \( \psi \) is the solution of the electronic Schrödinger Equation (1.1). It contains all information about the particular system. For example the shape of the molecule as well as its properties can be calculated from the wave function.

**Approximations of the Schrödinger Equation**

Various approximate solutions of the electronic Schrödinger Equation (1.1) are available. They are divided in two groups. On the one hand there are *ab initio* theories. They all have in common that the wave function \( \psi \) in the Schrödinger Equation (1.1) is approximated. On the other hand is Density Functional Theory (DFT). In DFT the Hamilton operator, \( \hat{H} \) in the Schrödinger Equation (1.1), is approximated.

**Successes and goals in Quantum Chemistry**

The correct prediction of the equilibrium geometric structure of molecules was the first success in Quantum Chemistry. Calculated
bond lengths and angles are in agreement with the ones experimentally found. Thermodynamic data like bond energies are calculated with great accuracy. Even transition states are reproduced correctly. At present, two goals are pursued. The breaking and forming of a chemical bond still presents a great problem. Thus, the description of a chemical reaction is cumbersome. On the other hand the reaction of a molecule to a beam of light, for example a laser, is calculated incorrectly. The source of these failures is the correlation energy.

HF

The best known \textit{ab initio} theory is Hartree Fock (HF) theory. The wavefunction, $\psi$, in the Schrödinger Equation (1.1) is approximated with a simple function, a single Slater determinant. The difference of the true energy, $E$ in equation (1.1), and the HF energy is called correlation energy. While HF gives good results for atoms, it shows large errors for chemical bonds.

DFT

Part I of this work deals with Density Functional Theory (DFT). The electron density gives the probability of finding an electron at a given point in space. It is one central ingredient in DFT. The other ingredient is the energy functional. The energy of a molecule is calculated from the energy functional. It utilizes the electron density as input. The correlation energy in DFT is similar to the one in HF but not identical (see Ref. [7] and Section 1.6).

Research in DFT centers around finding better energy functionals. It is believed that a new generation of functionals, called orbital dependent [8, 9, 10, 11, 12] functionals, will provide better results. Part I of this work investigates Orbital Dependent Functionals (ODF) in DFT.
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DMFT
Density Matrix Functional Theory (DMFT) is a more recently developed theory. Like in DFT the energy functional is approximated. As input a rather abstract function is used, the one-electron reduced density matrix (1-RDM). Only simple functionals have been proposed so far. A recently [13] developed functional excellently describes the breaking and forming of a chemical bond. This functional is further refined in Part II of this work.

Results of this work
This work deals with Electron Correlation in Orbital Dependent Functionals (ODF). Part I of this work is devoted to DFT and Part II deals with DMFT. They are connected by ODF which appear in both theories. Part I presents problems associated with ODFs in DFT. Not all of them can be solved. It is suggested to use ODFs in DMFT instead. Part II presents a promising DMFT functional.

1.2 Orbital Dependent Functionals (ODF) in Density Functional Theory (DFT)

Hohenberg and Kohn theorem
Density Functional Theory (DFT) (see Section 2.1) represents one particular electronic structure theory. Hohenberg and Kohn [14] introduced DFT in 1964. They proved that there is a one-to-one mapping between the ground state wave function, $\psi_{\text{elec}}(x_1, \ldots, x_N)$, and the ground state electron density, $\rho_{\text{elec}}(r)$. As a result the total energy, $E_{\text{elec}}$, can be expressed as a functional of the electron density (Equation (1.21)). The main merit of DFT is the reduction of the number of variables. The electron density depends only on three coordinates, namely, the spatial coordinates. The main downside
of DFT is the energy functional. Its exact form is unknown.

**Kohn and Sham Theorem**

Kohn and Sham [15] presented the most successful realization of DFT (KS DFT, discussed in Section 2.2). They introduced a non-interacting particle system that shares the same density with the exact system. This results in a break up of the energy functional into different parts, of which only one is unknown. The famous exchange correlation (xc) functional collects all unknown residues of the total energy. Research in KS DFT centers around development of accurate xc functionals that are computationally cheap. Development of xc functionals has been compared to “Jacob’s ladder” [16], indicating the impossibility to reach the exact functional.

**Kohn Sham and Exchange Correlation Potential**

The electrons in the KS system all feel the same local potential, the KS potential. The KS operator is formed from the kinetic operator and the KS potential. The eigenfunctions of the KS operator are the KS orbitals. The KS potential is such that the resulting ground state electron density is equal to the exact ground state electron density. The ground state electron density is calculated from the KS orbitals. The KS potential is split up in three parts. The external potential is the sum of the external field and the field introduced by the nuclei. The Coulomb potential is the Coulombic interaction of the electron density with itself. Finally, the exchange correlation (xc) potential is defined as the derivative of the xc functional with respect to the electron density evaluated with the exact electron density. Section 2.3 discusses the KS and xc potential.

**Current functionals**

The first step towards the exact functional was taken by Kohn and Sham [15]. The Local Density Approximation (LDA) employs the
uniform electron gas model. Despite its simplicity it was and still is successfully used in solid state physics. The family of LDAs is described in Section 2.4.1.

Generalized Gradient Approximations (GGA, discussed in Section 2.4.2) represent the second step. In addition to the electron density they include also the gradient of the density. In particular the hybrid functionals, discussed in Section 2.4.2, have been successfully applied to molecules. Finally, Meta- and Hyper-GGAs (Section 2.4.2) were introduced. All GGAs share an amazing accuracy at low computational costs. Despite their dominant position GGAs show plenty of shortcomings.

Deficiencies of current functionals
The deficiencies of GGAs can be divided into two groups. On the one hand electron correlation is not described correctly. While a great part of dynamical correlation is recovered a small amount of it is still missing. Consequently, weak interactions are calculated incorrectly. Dispersion forces and van der Waals interactions are impossible to treat. The non-dynamical or static part of correlation is notoriously difficult to account for. The lack of static correlation is the source of a crucial shortcoming. The binding energies of even small systems show large errors. This is exemplified by the H$_2$ dissociation curve.

On the other hand the GGA potentials are qualitatively wrong. In the molecular region they are not deep enough and in the asymptotic region they decay too fast. As a consequence, the energy difference between occupied and Rydberg orbitals is too small. Also the band gap, an important property in solid state physics, is reproduced incorrectly. Time Dependent DFT (TD DFT) describes response properties and excitations. TD DFT methods take orbitals and orbital energies as input. Therefore they suffer directly from
shortcomings in GGA potentials.

**ODF cure the deficiencies**

Orbital Dependent Functionals (ODF) present a remedy to the above mentioned shortcomings [8, 9, 10, 11, 12]. It is believed that ODF can be developed that reproduce both, static and dynamic correlation. Another advantage of ODF is the correct asymptotic behavior of their potential. In order to overcome the problems of LDA and GGA approaches, new variables are introduced in the functional definition. LDA and GGA are functionals of the electron density. In contrast, ODF employ KS orbitals and orbital energies as variables. Even virtual orbitals can enter the energy definition.

**Types of ODF**

ODF are the central subject of this work. The simplest ODF, the exact exchange functional (EXX), is presented in Section 2.5.1. EXX shares the same energy definition with Hartree-Fock (HF). The orbitals, however must be solutions of a local potential. This presents an additional constraint compared to the HF orbitals. Consequently, the EXX energy is strictly higher than the HF energy. While EXX is not expected to solve any of the problems associated with GGA functionals, it is perfectly suited as a simple test case [9].

A whole family of ODF can be deduced from perturbation theory (PT). Originally, these functionals are not meant to be used in a self consistent approach. Nevertheless, they have been proposed as a route towards better functionals [12, 17]. In Section 2.5.2 the second order perturbation theory functional (PT2) is presented. The difference of orbital energies appears in the denominator. Consequently, a (near) degeneracy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO) yields a collapse of the total energy. This is expected for the dissociation
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limit of H₂ but has also been established for CO, HF, N₂ and H₂O [11].

Finally, in Section 2.5.3 a family of ODF is presented. Its development was inspired by Density Matrix Functional Theory (DMFT, discussed in Part II). In the context of KS DFT the occupations are parametrized by the orbital energies. Hence, the KS DFT version of the functional is called CH-ε (see Section 2.5.3). This set of ODFs was believed to be the most promising route to better functionals in DFT [9, 18, 19].

Problem of ODF
With the introduction of ODF a new difficulty arises. Within the KS method the functional derivative of the xc functional is a central quantity. The derivative with respect to the electron density is called xc potential. The calculation of the LDA and GGA is simple, due to the direct dependence on the electron density. ODF, however, do not directly depend on the electron density. Its functional derivative cannot be calculated straightforwardly.

OEP and finite bases
The Optimized Effective Potential (OEP) [20, 21] is a method to calculate the functional derivative of an ODF. Section 2.6 gives the derivation of the OEP equations. The xc potential is written as an integral equation. Solving the OEP equations has proved to be a difficult task. The problem is to invert the response function, that appears in the OEP equations. The EXX functional, being the simplest ODF, is used to test methods to solve the OEP equations. Talman and Shadwick [21, 22] inverted the response function on a grid. This scheme is restricted to atoms, however.

Introducing a finite orbital set adds to the difficulties. It can be shown, that the OEP equations are an ill-posed problem, while there is a unique solution in the complete basis set limit [23]. Hence,
1.2. ORBITAL DEPENDENT FUNCTIONALS IN DENSITY FUNCTIONAL THEORY

the task is to develop a scheme that reproduces the solution of the complete basis set limit, while utilizing only finite orbital sets.

Approximations to OEP

Different approximate methods based on inversion of the response function are available. Sharp and Horton [20] suggest a crude approximation to Green’s function. Surprisingly, this approximation yields the good-quality exchange potential \( v_{xc}^{KLI}(r) \) of the Krieger, Li and Iafrate (KLI) method [24]. A more physically reasonable common energy denominator approximation (CEDA) has been applied to the orbital Green’s function [25]. The same potential, \( v_{xc}^{CEDA}(r) \) has been obtained by Della Salla and Görling [26] within the localized Hartree-Fock (LHF) approximation. Izmaylov et. al. [27] obtained the CEDA potential in the effective local potential (ELP) approach. The full OEP solution is obtained by improving on the KLI method [28]. Kümmel and Perdew [29] developed a numerical procedure to refine the KLI/CEDA potential.

Basis set schemes for OEP

To solve the OEP equations without approximations an additional basis set is introduced. The response function is expanded in a (necessarily) finite basis set. Together with a (necessarily) finite orbital set a matrix representation of the response function is obtained. The response matrix is inverted with a singular value decomposition (SVD). The crucial point is the cutoff criterion which distinguishes linear dependency from independency. This method was implemented by different authors [23, 30, 31]. Results obtained by this method agree with the numerically derived values of Talman [21, 32].

A different method to solve the OEP equations introduces a basis set for the potential [33, 34, 35, 36]. The expansion coefficients for the potential basis are minimized directly. In particular, Yang and
co-workers have recently developed this method [11, 37, 38, 39]. Applications of this method to the EXX functional raised doubts about the applicability of the OEP method. Staroverov et. al. [40] found wildly oscillating local exchange potentials yielding HF total energies and densities. As mentioned above the EXX energy is expected to be strictly above the HF energy. In Reference [40] it is argued, that with a finite orbital set equality of EXX and HF can always be achieved. Reference [41] discusses the sufficient conditions.

**Balancing schemes**
In the light of the results of Reference [40] different authors propose a balancing of orbital and potential basis [23, 42, 43]. It is advocated that the potential basis must be (much) smaller than the orbital basis.

Reference [42] utilizes the self consistent scheme described in Section 2.6.1. Starting from the same basis set for orbitals and potential the orbital set is augmented and the potential set is truncated. The potential and orbital bases are considered balanced if the matrix elements of the response matrix have converged. In addition the difference of EXX and HF energies is monitored.

In Reference [43] the direct optimization scheme is utilized. The expansion coefficients of the potential basis are collected in a solution vector. For a given orbital basis the potential basis is enlarged. The length of the solution vector remains “small” and “constant” until a sharp increase is observed. The largest potential basis that still yields a solution vector with “small” length is considered to be balanced with respect to the given orbital set.

**Criticism of basis set schemes for OEP**
The proposed basis set schemes [23, 30, 31, 42, 43] agree well with the numerically obtained values of Talman [21, 32]. Also the pub-
lished orbital spectra show only small deviations from the numerical results. Nevertheless, all basis set schemes suffer from a crucial downside. In the SVD scheme a reliable cutoff criterion must be found. For the balancing schemes a potential basis must be chosen. The non-uniqueness of the different schemes shows up in the calculated total energies for EXX. Different OEP schemes give different total energies. In the cases of CO and N₂ [42, 44, 45] the published total energies differ by ca. 1mH. Moreover, it appears that the differences increases with increasing $E_{\text{EXX}} - E^{HF}$ (see Table III in Reference [45]).

**Results of Part I: Virtual orbitals must enter all parts of the energy**

Part I presents the results of Orbital Dependend Functionals (ODF) in Density Functional Theory (DFT). In Chapter 3 collapse of PT2 and CH-ε is shown. Utilizing a large potential basis and a small orbital basis an oscillating potential is obtained. It yields a (near) degeneracy of highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO). Consequently, the total energy of PT2 collapses and a break down of the CH-ε energy is found.

Chapter 4 presents a first contribution to the efforts [23, 30, 31, 42, 43, 45] to cure the problems of finite basis set Optimized Effective Potential (OEP) methods. A balancing of orbital and potential basis is advocated. More elaborate schemes are put forward by different authors. The effect of the reference potential is analyzed.

In Chapter 5 balanced basis sets based on basis sets of Reference [42] are used for CH calculations on Be and Ne. In contrast to unbalanced basis sets reasonable total energies are obtained. The full KS potential is well behaved. Large oscillations are not observed. However, the orbital spectrum is deficient. Unphysical degeneracies are observed. Inclusion of virtual orbitals in all terms of the energy
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functional yields a well-behaved potential and orbital spectrum.

In conclusion of Part I it is advocated to include virtual orbitals in all parts of the energy functional. Density Matrix Functional Theory, which includes virtual orbitals in all parts of the energy functional is an obvious next step.

Results of Chapter 3: Collapse of GLPT2 and breakdown of CH-ε

In Chapter 3 results are presented that build upon the findings of Staroverov et. al. In Section 3.1 it is shown, using similar arguments as in Reference [40], that exact degeneracy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO) can artificially be constructed, if a finite orbital basis set is used. Two different potentials with virtually zero difference of HOMO and LUMO for the He atom are presented. The bizarre shape of the orbitals is discussed and the components of the respective orbital energies are analyzed.

Section 3.2 discusses the consequences for the PT2 functional introduced in Section 2.5.2. Equations for the two-electron case are presented. It is pointed out, that the GLPT2-OEP energy collapses with the potentials presented in Section 3.1. This contradicts the findings in Reference [11, 17].

In Section 3.3 it is demonstrated that the problems are not peculiar to perturbation theoretic expressions. The CH-ε functional presented in Section 2.5.3 yields unphysically low total energies when the involvement of the virtual orbitals depends on the orbital energies. The total energy breaks down to less than -9 Hartree for He, where the full CI value is calculated to be -2.9 H. It is noted, that the breakdown wouldn’t appear if virtual orbitals were included in all terms of the energy functional.

Results of Chapter 4: A judicious choice of bases and reference
1.2. ORBITAL DEPENDENT FUNCTIONALS IN DENSITY FUNCTIONAL THEORY

Potential yield good quality results

Chapter 4 provides a first step towards a stable solution of OEP. It is argued that the potential and orbital basis sets must be balanced. This is demonstrated with the EXX functional for the two-electron case. For He and H₂ the correct OEP is known even in a finite basis set. For Be it is shown that the correct total energy can be reproduced. A judicious choice of reference potential yields good orbital energies.

Section 4.2 analyzes the interdependence of orbital and potential basis. In order to reproduce the correct total energy in a given basis with high numerical precision, at least the same quality basis sets are required for the orbitals and the potential. However, a physically meaningful accuracy is already achieved with a much smaller basis.

Section 4.3 focuses on the orbital energies. Only by imposing an exact condition large shifts of orbital energies can be prevented. Correct benchmark orbital energies are used to investigate the effect of different reference potentials. The dependence of notably the energies of virtual orbitals on the reference potential surfaces. This is demonstrated for Be.

Results of Chapter 5: Balanced basis sets yield HOMO-LUMO degeneracy.

Chapter 5 investigates the effects of balanced basis sets on CH-ε. Balanced basis sets based on balanced sets from Reference [42] are employed. While the total energy is stable, orbital energies are unphysical. Too low virtual orbital energies are observed, culminating in a HOMO-LUMO degeneracy for Be and Ne. Consequently, the variational collapse of the GLPT2 functional is established. It is argued that virtual orbitals must enter all parts of the energy functional, as is the case in DMFT. This argument is supported
by investigating an energy functional that includes virtual orbitals in all parts. A finite HOMO-LUMO gap is found, but still virtual orbital energies are too low.

Section 5.1 describes the employed method. The charge density constraint from Reference [42] is adapted to the direct minimization method. The analog of Koopmans’ theorem [46] is imposed. The HOMO energy must equal the negative ionization potential. This prevents a large shift in orbital energies as seen in Chapter 4. The balanced basis sets of Reference [42] are employed. Since the CH-\(\epsilon\) functional depends on virtual orbitals the orbital set for Be is augmented with p functions. Exponents for the orbital basis set used in that Chapter are presented.

Section 5.2 presents the results for Be and Ne. The total energy of Be is in reasonable agreement with the full CI energy. A smooth, well-behaved potential is obtained. Large shifts in the orbital spectrum are prevented by enforcing the KS analogue of Koopmans’ theorem. This provides a major improvement of the results found in Chapter 3. However, the virtual orbital spectrum is deficient. Degeneracy of 2s (HOMO) and 2p (LUMO) orbitals is found.

In the case of Ne oscillations in the potential are observed. The 3s orbital becomes occupied leaving the set of 2p orbitals to represent both HOMO and LUMO. Consequently, a degeneracy of HOMO and LUMO is found. Occupying the 3s orbital influences the total energy. It is 2 Hartree higher than the full CI energy.

Section 5.3 presents a new functional. In an ad-hoc manner the fictitious occupation numbers of the CH functional are included in all parts of the energy functional. This leads to a well-behaved potential and a surprisingly good total energy. A finite HOMO-LUMO gap is observed. Nevertheless, virtual orbital energies are too low.
Gilbert Theorem
In Density Matrix Functional Theory (DMFT) there is an analogue to the Theorems of Hohenberg and Kohn. Gilbert [47] proved an extension of the Hohenberg-Kohn theorems. A one-to-one mapping between the ground state one particle reduced density matrix (1-RDM) and the ground state wave function was established. Consequently, the total energy can be expressed as a functional of the 1-RDM. Like in DFT a variational principle is established.

Difference between DFT and DMFT
DMFT provides a crucial advantage over DFT. The exact kinetic energy functional is known. Consequently, introduction of a non-interacting particle system like in KS DFT is avoided. Like in KS DFT, orbitals appear in DMFT. They are called natural orbitals (NO). In contrast to KS DFT, the natural occupation numbers take values between zero and one. Orbitals occupied with less than half an electron will be denoted virtual or weakly occupied orbitals. Occupied or strongly occupied orbitals have occupation numbers of more than half an electron. DMFT shares a crucial disadvantage with DFT. The exact form of the exchange correlation functional is not known.

Available Functionals: Löwdin Shull
Löwdin and Shull [48] (see Section 7.1) derived a functional for the two-electron case. The authors proved that the exact two-electron closed-shell wave function reduces to just a summation over excited closed-shell configurations, when the NO are used as an expansion basis. The corresponding xc functional employs exchange integrals
multiplied with the square root of the natural occupation numbers. The integral is assigned a negative sign if an occupied and unoccupied orbital enters, a positive sign otherwise. The functional is exact for most two-electron systems.

**Available Functionals: CH**

Thus far, only a few approximate functionals have been proposed. All of them belong to the group of so-called “primitive functionals”, which employ only Coulomb and exchange-like integrals. The first approximate functional was derived independently by Müller [49] and Buijse and Baerends [50] (see Section 7.3). Csanyi an Arias [51] gave this functional the name Corrected Hartree (CH). CH employs the Coulomb integrals as well as exchange integrals. All exchange integrals are multiplied with minus the square root of the respective natural occupation numbers. The dissociation curve of H\(_2\) is qualitatively reproduced correctly [13].

**Available Functionals: GU**

Goedecker and Umrigar [52] (see Section 7.4) modified the CH functional by omitting all diagonal Coulomb and exchange integrals. As a consequence the total energies for atoms and molecules around the equilibrium distance improve. However, at large interatomic distances the quality of the results deteriorates [53, 54, 55].

**Available Functionals: C1, C2 and C3**

Recently [13], a serie of three repulsive corrections C1, C2, and C3 to the CH functional was proposed. The first correction, C1 (see Section 7.5.1), restores the +1 factors in front of the square root for the virtual-virtual terms. The second correction, C2 (see Section 7.5.2), changes the interaction between different occupied orbitals to NOs to an exchange type interaction. The third correction, C3 (see Section 7.5.3), introduces explicitly a special treatment of strong
1.3. ORBITAL DEPENDENT FUNCTIONALS IN DENSITY MATRIX FUNCTIONAL THEORY

(nondynamical) correlation. This requires a preselection of bonding and anti-bonding orbitals.

Available Functionals: PNOF

Piris and Leiva [56, 57] (see Section 7.6) proposed the Piris natural orbital functional (PNOF0), based on a detailed consideration of properties of the cumulant. The PNOF0 functional effectively applies the C1 correction in combination with the diagonal GU correction. Piris [56] has also introduced an extended form, denoted PNOF, which prevents pinning of high occupation number at integer value. Lathiotakis and Marques [58] have shown in benchmark calculations that the simple PNOF0 form performs better than PNOF.

Available Functionals: ML

In Ref. [59] (see Section 7.7) a new functional is proposed by Marques and Lathiotakis (ML). In this functional the square root factor in the CH functional is replaced with the Padé approximant in the product of NO occupations. The coefficients in the approximant being empiracally determined by a fit to reproduce the correlation energies of prototype molecules at equilibrium geometry. The Padé approximant form implies that only integer powers of the NO occupations are employed in both numerator and denominator.

Results of Chapter 8: Excellent results for AC3

In Chapter 8 a DMFT functional with a fully automatic, occupation number driven, determination of the (approximate) matrix elements of the two-density cumulant is presented. Unlike C3, the proposed AC3 does not require the manual selection of the bonding and antibonding natural orbitals of a bond. AC3 reproduces well the reference potential curves of the multireference configuration interaction method for all interatomic distances X-H for CH₄,
NH₃, H₂O and HF. The H₂ potential energy curve has a spurious maximum at ca. 4 Bohr. However, the correct dissociation limit is delivered.

The results are compared to PNOF0, ML, HF and a GGA. None of the four methods correctly reproduce the dissociation limit of the potential energy curves. PNOF0 and ML are very good at equilibrium distance.

1.4 The Schrödinger Equation

At the very heart of quantum mechanics stands the Schrödinger Equation. It describes any microscopic system. The solution of the Schrödinger Equation will provide us with everything we can know about the system. Its non-relativistic version is cast in the form

\[
\hat{H}(t) \Psi (X_1, \ldots, X_M, x_1, \ldots, x_N, t) = i \frac{\partial}{\partial t} \Psi (X_1, \ldots, X_M, x_1, \ldots, x_N, t) 
\]

where the operator is defined as

\[
\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W} 
\]

\[
\hat{T} = -\frac{1}{2} \left[ \sum_A^M \nabla_A^2 + \sum_i^N \nabla_i^2 \right] 
\]

\[
\hat{V}(t) = \sum_A^M Z_A v_{\text{ext}} (R_A, t) - \sum_i^N v_{\text{ext}} (r_i, t) 
\]

\[
\hat{W} = \sum_{A,B}^M \frac{Z_A Z_B}{|R_A - R_B|} + \sum_{i,j}^N \frac{1}{|r_i - r_j|} 
\]

\[
- \sum_{A,i}^M \frac{Z_A}{|R_A - r_i|} 
\]

\[
\]
1.4. THE SCHRÖDINGER EQUATION

The capital variables and indexes refer to nuclei and lower case variables and indexes refer to electrons. \( M \) is the number of atoms. In this equation and for the rest of this work \( N \) is the number of electrons of the system. The variables, \( X_i \) and \( x_i \), are composite variables of the spatial variables, \( R_i \) and \( r_i \), and the spin variables, \( S_i \) and \( s_i \). Solving Schrödinger’s Equation means finding the function \( \Psi (X_1, \ldots, X_M, x_1, \ldots, x_N, t) \). All properties of the system can be derived from the wave function.

In this work only stationary problems will be addressed. This leads to a time independent external field, \( \hat{V}(t) = \hat{V} \). Separating time from space is done by a product Ansatz for the wave function, \( \Psi (X_1, \ldots, X_M, x_1, \ldots, x_N, t) = \psi (X_1, \ldots, X_M, x_1, \ldots, x_N) f(t) \). After some manipulation of Equation (1.2) the time independent Schrödinger Equation is obtained

\[
\hat{H} \psi (X_1, \ldots, X_M, x_1, \ldots, x_N) = E \psi (X_1, \ldots, X_M, x_1, \ldots, x_N) \quad (1.7)
\]
\[
\hat{H} = \hat{T} + \hat{V} + \hat{W} \quad (1.8)
\]
\[
\hat{V} = \sum_A^{M} Z_A v_{ext} (R_A) - \sum_i^N v_{ext} (r_i) \quad (1.9)
\]

The total energy, \( E \), is a constant in the time independent Schrödinger Equation (1.7). Finding the eigenvalues and eigenfunctions of the time independent Hamilton operator, \( \hat{H} \), is equivalent to solving Equation (1.7). Again, all properties of the stationary system can be derived from the eigenfunctions, \( \psi (X_1, \ldots, X_M, x_1, \ldots, x_N) \).

Finally, the Born-Oppenheimer approximation is applied. Considering the large difference in mass between nuclei and electrons, the nuclei are treated as point charges, i.e. they are treated classically. Their interaction with the electrons is summed into the external field, \( v_{ext, elec} (r_1, \ldots, r_N) \).
CHAPTER 1. INTRODUCTION

\begin{equation}
\hat{H}_{elec} \psi_{elec} (x_1, \ldots, x_N) = E_{elec} \psi_{elec} (x_1, \ldots, x_N) \tag{1.10}
\end{equation}

\begin{equation}
\hat{H}_{elec} = \hat{T}_{elec} + \hat{V}_{elec} + \hat{W}_{elec} \tag{1.11}
\end{equation}

\begin{equation}
\hat{T}_{elec} = - \frac{1}{2} \sum_{i}^{N} \nabla_{i}^2 \tag{1.12}
\end{equation}

\begin{equation}
\hat{V}_{elec} = \sum_{i}^{N} v_{ext,elec} (r_1, \ldots, r_N) \tag{1.13}
\end{equation}

\begin{equation}
\hat{W}_{elec} = \sum_{i<j}^{N} \frac{1}{|r_i - r_j|} \tag{1.14}
\end{equation}

Equation (1.10) is called the exact non-relativistic stationary electronic Schrödinger Equation. In the rest of this work this equation is referred to as Schrödinger Equation. The eigenfunctions of the Schrödinger Equation (1.10) give all properties of the electronic system. The eigenfunction, \( \psi_{0,elec} \), with lowest eigenvalue, \( E_{0,elec} \), is called the ground state electronic wave function. In the rest of this work it will be called wave function and the subscripts “elec” and “0” are dropped.

Calculating eigenfunctions is a difficult task. However, there is another way to obtain wave function \( \psi (x_1, \ldots, x_N) \). The Rayleigh-Ritz variational principle ensures that the minimum of the expectation value of \( \hat{H} \) is obtained only at \( \psi (x_1, \ldots, x_N) \).

\begin{equation}
E \leq \frac{\langle \phi | \hat{H}_{elec} | \phi \rangle}{\langle \phi | \phi \rangle} \tag{1.15}
\end{equation}

Equality holds only if \( \phi (x_1, \ldots, x_N) = \psi (x_1, \ldots, x_N) \).
1.5. The Density Matrix and the Electron Density

The wave function is not an observable. To obtain an observable from the wave function another quantity is introduced. The \(N\)-particle density matrix is defined as

\[
\Gamma^N \left( x_1', \ldots, x_N', x_1, \ldots, x_N \right) = \psi^* (x_1', \ldots, x_N') \psi (x_1, \ldots, x_N) \tag{1.16}
\]

The diagonal part of the \(N\)-particle density matrix (Equation (1.16)) gives the probability of finding one electron at each position-spin point \(x_i\) simultaneously.

\[
\Gamma^N (x_1, \ldots, x_N) = \psi^* (x_1, \ldots, x_N) \psi (x_1, \ldots, x_N) \tag{1.17}
\]

Integration over \(M\) variables of the \(N\)-particle density matrix gives the \((N-M)\) particle reduced density matrix.

\[
\Gamma^{N-M} (x_1, \ldots, x_{N-M}) = \binom{N}{M} \int \Gamma^N (x_1, \ldots, x_N) \, dx_{N-M+1} \ldots dx_N \tag{1.18}
\]

1.5.1 The pair density

The pair density is the central quantity to describe electron correlation.

\[
\Gamma^2 (x_1, x_2) = \frac{N(N-1)}{2} \int \Gamma^N (x_1, \ldots, x_N) \, dx_3 \ldots dx_N \tag{1.19}
\]
Chapter 1. Introduction

It represents the probability of finding one electron at position-spin \(x_1\) and one electron at position-spin \(x_2\) simultaneously. The exact ground state pair density is sufficient to calculate the ground state energy, since the Hamiltonian in equation (1.10) is a two particle operator.

1.5.2 The one-particle reduced density matrix (1-RDM)

Part II of this work deals with Density Matrix Functional Theory. Gilbert [47] showed that there is a one-to-one mapping between the ground state wave function \(\psi_0\) and the ground state one-electron reduced density matrix (1-RDM) \(\gamma_0\) (see equation (1.20)). Consequently, the pair density is approximated with a function of the 1-RDM.

\[
\gamma(x'_1, x_1) = N \int \Gamma^N(x'_1, x_2, \ldots, x_N, x_1, \ldots, x_N) \, dx_2 \ldots dx_N \tag{1.20}
\]

1.5.3 The electron probability density

The electron probability density is the diagonal part of 1-RDM integrated over spin.

\[
\rho(r) = \int \gamma(x_1, x_1) \, ds_1 \tag{1.21}
\]

The electron probability density gives the probability of finding an electron at point \(r\) in space. It is usually called the electron density. Hohenberg and Kohn [14] proved that there is a one-to-one mapping between the ground state wave function \(\psi_0\) and the ground state density \(\rho_0\). This is the foundation of Density Functional Theory (DFT), the topic of Part I.
1.6 Correlation Energy

In this Section definitions of correlation energy for different theories are given. A rigorous separation of static and dynamic correlation, however, is not possible.

1.6.1 Exact Correlation

Assume that for a given system the ground state wave function \( \psi_0 \) is known. The ground state pair density \( \Gamma_0^2(1, 2) \), ground state 1-RDM \( \gamma_0(1, 2) \) and the ground state density \( \rho_0(1) \) are then calculated from Equations (1.19), (1.20) and (1.21), respectively. The variables \( i \) refer to the position-spin variable \( x_i \). The ground state energy is calculated from (1.22).

\[
E_0 = \langle \hat{T} \rangle + \langle \hat{V} \rangle + \langle \hat{W} \rangle \\
= -\frac{1}{2} \int_{1 \rightarrow 1'} \nabla^2 \gamma_0(1, 1') d1 + \int \rho_0(r_1) v(r_1) d1 \\
+ \frac{1}{2} \int \frac{1}{r_{12}} \Gamma_0^2(1, 2) d1 d2
\]

The ground state pair density \( \Gamma_0^2(1, 2) \) may be broken up into the Coulomb part, which is the product of the one-electron probabilities \( \rho_0(1) \rho_0(2) \), and the exchange part expressed by the 1-RDM and the correlation part, implicitly defined by equation (1.23).

\[
\Gamma^2(1, 2) = \rho_0(1) \rho_0(2) - |\gamma_0(1, 2)| + \Gamma_c^2(1, 2)
\]

The expectation values (1.24), (1.25) and (1.26) are called Coulomb energy, exchange energy and correlation energy, respectively.
CHAPTER 1. INTRODUCTION

\[ E_{\text{coul}} = \frac{1}{2} \int \frac{\rho_0 (1) \rho_0 (2)}{r_{12}} d1d2 \]  
(1.24)

\[ E_x = -\frac{1}{2} \int \frac{|\gamma_0 (1, 2)|^2}{r_{12}} d1d2 \]  
(1.25)

\[ E_{\text{corr}} = \frac{1}{2} \int \frac{\Gamma^2_0 (1, 2)}{r_{12}} d1d2 \]  
(1.26)

1.6.2 Correlation Energy with HF reference

In HF the expectation value of the Hamiltonian (1.10) is minimized with a single Slater determinant. The corresponding ground state pair density \( \Gamma^2_{0, HF} (1, 2) \), ground state 1-RDM \( \gamma^H_F (1, 2) \) and the ground state density \( \rho_0^{HF} (1) \) are then calculated from Equations (1.19), (1.20) and (1.21), respectively. The correlation energy with HF reference \( E_{\text{corr}}^{HF} \) is the difference to the exact ground state energy.

\[
E_{\text{corr}}^{HF} = E_0 - \langle E^{HF} \rangle \\
= -\frac{1}{2} \int_{1 \rightarrow 1'} \nabla^2 \left( \gamma_0 (1, 1') - \gamma^H_F (1, 1') \right) d1 \\
+ \int \left( \rho_0 (1) - \rho_0^{HF} (1) \right) v (1) d1 \\
+ \frac{1}{2} \int \frac{1}{r_{12}} \left( \Gamma^2_0 (1, 2) - \Gamma^2_{0, HF} (1, 2) \right) d1d2 
\]  
(1.27)

It is noted that the correlation energy includes contributions from the kinetic, potential and electron-electron interaction energies.

1.6.3 Correlation Energy in KS DFT

As was mentioned in Section 1.2 there is a functional of the ground state density \( \rho_0 (r) \). Following Kohn and Sham [15] (see also Section
2.2) the ground state KS wave function $\psi_0^{KS}$ yields the exact ground state electron density $\rho_0$, via equation (1.21). The ground state KS 1-RDM is calculated from equation (1.20) The expectation value of the Hamiltonian (1.10) with the KS wave function is the KS determinantal energy $E^{KS}$.

$$E^{KS} = \int_{1\rightarrow1'} \gamma^K_0 (1, 1') \, d1 + \int \rho_0 (1) \, v (1) \, d1$$
$$+ \frac{1}{4} \int \frac{2\rho_0 (1) \rho_0 (2) - \left| \gamma^K_0 (1, 2) \right|^2}{r_{12}} \, d1 \, d2$$  \hspace{1cm} (1.28)

Subtraction of the KS determinantal energy $E^{KS}$ (equation (1.28)) from the exact energy $E_0$ (equation (1.22)) yields the correlation energy in KS DFT.

$$E^{KS}_{DFT, corr} = \langle T \rangle - T_s + \langle W \rangle - \frac{1}{4} \int \frac{2\rho_0 (1) \rho_0 (2) - \left| \gamma^K_0 (1, 2) \right|^2}{r_{12}} \, d1 \, d2$$  \hspace{1cm} (1.29)

The correlation energy in KS DFT includes only contributions from the kinetic energy and the electron-electron interaction energy. The nuclear-electron energy makes no contributions to the correlation energy in KS DFT, since the KS ground state density is equal to the exact ground state density (compare equations (1.22) and (1.28)).

### 1.6.4 Correlation Energy in DMFT

Gilbert [47] established the existence of a functional of the ground state 1-RDM. The pair density, $\Gamma^2(1, 2)$, is expressed by a function of the 1-RDM (see equation 1.23).

$$\Gamma^2(1, 2) = C(\gamma; 1, 2)$$  \hspace{1cm} (1.30)
The expectation value of function $C(\gamma; 1, 2)$ with the $\frac{1}{r_{12}}$ operator is called the correlation energy in DMFT.
Part I

Orbital Dependent Functionals in Density Functional Theory

Der Worte sind genug gewechselt,
Laßt mich auch endlich Thaten sehn;
Indeß ihr Complimente drechselt,
Kann etwas nützliches geschehn.

(Director in Faust: Der Tragödie erster Teil
by J.W. von Goethe (1808))
In the first three sections the concepts and Equations of DFT are presented. The proofs given by Hohenberg and Kohn [14] are reviewed in Section 2.1. It is shown that there is a functional of the electron density and that its global minimum gives the correct total energy. Section 2.2 contains a summary of the concepts of Kohn Sham DFT (KS DFT) [15]. The KS system of non-interacting particles is introduced. The exchange correlation (xc) functional, the central quantity of KS DFT, is defined. The theoretical part of DFT ends with Section 2.3. The KS potential and the xc potential are discussed. Various available approximations to the xc functional are presented in Section 2.4. An overview of Orbital Dependent Functionals is given in Section 2.5. The Optimized Effective Potential method (OEP) is introduced in Section 2.6

2.1 Density Functional Theory (DFT)

Density Functional Theory (DFT) was introduced in 1964 by Hohenberg and Kohn [14]. They proved that there is an energy functional of the electron density. It yields the exact total energy, if evaluated at the exact electron density. The theorem is stated as a mere existence proof. It is known as the first Hohenberg Kohn theorem and will be discussed in Section 2.1.1. The energy functional
CHAPTER 2. THEORY

could be shown to have a global minimum. The global minimum is unique and yields the exact total energy. This is summarized in the second Hohenberg Kohn theorem. It will be discussed in Section 2.1.2

2.1.1 First Hohenberg-Kohn Theorem

The first Hohenberg-Kohn theorem establishes a one-to-one mapping between the ground state electron density, the ground state wave function and the external potential. Moreover, it states that there is an energy functional of the density. This is usually depicted as

$$\rho_0 (r) \Leftrightarrow \psi_0 (r_1, \ldots, r_N) \Leftrightarrow v_{ext} (r) \Rightarrow E_0$$

In the remainder of this Section this statement is proven by *reductio ad absurdum*.

Assume there are two differing (by more than a constant) external potentials, $v(r)$ and $v'(r)$, which give rise to two differing (by more than a phase factor) wave functions $\psi_0 (r_1, \ldots, r_N)$ and $\psi'_0 (r_1, \ldots, r_N)$. Assume both wave functions yield the same electron density.

$$v(r) \Rightarrow \hat{H} \Rightarrow \psi_0 (r_1, \ldots, r_N) \Rightarrow \rho_0 (r)$$

and

$$v'(r) \Rightarrow \hat{H}' \Rightarrow \psi'_0 (r_1, \ldots, r_N) \Rightarrow \rho_0 (r)$$

The wave function $\psi'_0 (r_1, \ldots, r_N)$ is used as a trial wave function for $\hat{H}$. According to the Rayleigh-Ritz variational principle it is found
2.1. DENSITY FUNCTIONAL THEORY

\[ E_0 < \langle \psi'_0 \mid \hat{H} \mid \psi'_0 \rangle \]  \hspace{1cm} (2.1)

\[ = \langle \psi'_0 \mid \hat{H}' \mid \psi'_0 \rangle + \langle \psi'_0 \mid \hat{H} - \hat{H}' \mid \psi'_0 \rangle \]  \hspace{1cm} (2.2)

\[ \Leftrightarrow E_0 < E'_0 + \int \rho_0 (r) (v (r) - v' (r)) \, dr \]  \hspace{1cm} (2.3)

Interchanging the roles of primed and unprimed and applying the above mutatis mutandis it is found

\[ E'_0 < E_0 + \int \rho_0 (r) (v' (r) - v (r)) \, dr \]  \hspace{1cm} (2.4)

Adding Equation (2.3) and Equation (2.4) leads to the contradiction

\[ E_0 + E'_0 < E'_0 + E_0 \]  \hspace{1cm} (2.5)

\[ \Leftrightarrow 0 < 0 \]  \hspace{1cm} (2.6)

This concludes the prove for the first Hohenberg Kohn theorem. Pictorially speaking it is found that \( \rho_0 (r) \Rightarrow \psi_0 (r_1, \ldots, r_N) \Rightarrow v_{\text{ext}} (r) \Rightarrow E_0 \). The reverse is obvious, since the external potential uniquely defines the Hamiltonian, which defines the ground state wave function and the ground state electron density.

An energy functional of the ground state electron density can now be defined. It is divided into system dependent and independent parts. The latter is the famous Hohenberg Kohn functional.
E_v [\rho_0] = \int \rho_0 (r) v (r) \, dr + F_{HK} [\rho_0] \quad (2.7)

F_{HK} [\rho_0] = T [\rho_0] + W [\rho_0] \quad (2.8)

T [\rho_0] = \left\langle \psi_0 [\rho_0] \left| \hat{T} \right| \psi_0 [\rho_0] \right\rangle \quad (2.9)

W [\rho_0] = \left\langle \psi_0 [\rho_0] \left| \hat{W} \right| \psi_0 [\rho_0] \right\rangle \quad (2.10)

This completes the Section on the first Hohenberg Kohn theorem. It remains to mention that it holds only for ground states, which is the reason for the subscript 0 throughout the Equations.

2.1.2 Second Hohenberg-Kohn Theorem

The second Hohenberg Kohn theorem establishes a variational principle for the energy functional (2.7). It makes use of the Rayleigh-Ritz variational principle.

In the previous Section a one-to-one mapping was established between the electron density and the wave function. An arbitrary ground state density, \( \rho' (r) \), is used as a trial density for the energy functional \( E_v [\rho] \).

\[
E_v [\rho'] = \left\langle \psi'_0 \left| \hat{H} \right| \psi'_0 \right\rangle \quad (2.11)
\]

\[
\geq \left\langle \psi_0 \left| \hat{H} \right| \psi_0 \right\rangle = E_v [\rho_0] \quad (2.12)
\]

This concludes the proof that there is a global minimum for the exact functional, \( E_v [\rho] \).
2.2 Kohn Sham DFT (KS DFT)

This Section presents the Kohn Sham (KS) approach to DFT [15]. In Section 2.2.1 the KS system is introduced. It is a system of non-interacting electrons. As a result the energy functional (2.7) is divided into four parts. The kinetic energy of the non-interacting electrons, the interaction energy with the external field, the Coulomb energy and a remainder. The remainder is called exchange correlation (xc) functional. It collects all terms that are missing to the exact energy. Section 2.2.2 presents the definition of the xc functional.

2.2.1 The Kohn Sham System

A non-interacting particle system consists of electrons, which do not interact via the electron-electron operator, \( \hat{W} \). The Kohn Sham system is a system of non-interacting particles that shares the same density with the exact system. The Kohn Sham Equations read

\[
\left\{-\frac{1}{2} \nabla^2 + v_s(r)\right\} \phi_i(r) = \varepsilon_i \phi_i(r) \tag{2.13}
\]

The eigenfunctions, \( \phi_i(r) \), are called KS orbitals and the eigenvalues, \( \varepsilon_i \), are the KS orbital energies. The ground state density is calculated from the N orbitals with lowest orbital energies as

\[
\rho_0(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 \tag{2.14}
\]

The Kohn Sham Potential, \( v_s(r) \), is such that Equation 2.14 holds. In Section 2.3 it is shown how to obtain an expression for approximate potentials.
2.2.2 The Exchange Correlation (XC) Functional

With the introduction of the non-interacting particle system the wave function is reintroduced in DFT. This gives the possibility to give an explicit expression for the energy. The idea is to calculate as much as possible exactly and approximate the rest. The rest is stored in the famous exchange correlation (xc) functional.

The energy functional (2.7) is manipulated by adding and subtracting the non-interacting kinetic energy and the Coulomb energy:

\[
E_v [\rho_0] = T_s [\rho_0] + E_{ext} [\rho_0] + E_{coul} [\rho_0] + E_{xc} [\rho_0]
\] (2.15)

\[
T_s [\rho_0] = -\frac{1}{2} \sum_i^N \int \phi_i^* (r) \nabla^2 \phi_i (r) \, dr
\] (2.16)

\[
E_{ext} [\rho_0] = \int \rho_0 (r) \psi_{ext} (r) \, dr
\] (2.17)

\[
E_{coul} [\rho_0] = \frac{1}{2} \int \int \frac{\rho_0 (r) \rho_0 (r')}{|r - r'|} \, dr \, dr'
\] (2.18)

\[
E_{xc} [\rho_0] = F_{HK} [\rho_0] - \frac{1}{2} \int \int \frac{\rho_0 (r) \rho_0 (r')}{|r - r'|} \, dr \, dr' - T_s [\rho_0]
\] (2.19)

The Equations above implicitly define the xc functional, \( E_{xc} [\rho] \). It is the junkyard for all energy contributions that are unknown. Approximations to the xc functional are presented in Section 2.4.

2.3 The Kohn Sham and Exchange Correlation Potential

This Section analyzes the KS potential. As was noted before (Section 2.2.1) the KS potential yields the exact ground state density.
2.3. THE KOHN SHAM AND EXCHANGE CORRELATION POTENTIAL

Using this constraint an explicit formula is given. It is decomposed in three parts, external potential, Coulomb potential and xc potential. The latter is given as the functional derivative of the xc functional.

2.3.1 Expression for the Kohn Sham potential

The KS potential is that potential that yields the exact density via Equations (2.13) and (2.14). The exact density gives the minimum for the energy functional (2.7). Consequently, a variation in the density must vanish.

\[
0 = \delta E_v = \delta T_s + \int \delta \rho(r) \left[ v_0(r) + \int \frac{\rho_0(r')}{|r - r'|} dr' + v_{xc}(r) \right] dr \quad (2.20)
\]

\[
\delta T_s = - \int v_s(r) \delta \rho(r) dr \quad (2.21)
\]

\[
v_{xc}(r) := \frac{\delta E_{xc}}{\delta \rho(r)} \bigg|_{\rho_0(r)} \quad (2.22)
\]

Where \( v_0(r) \) is the external potential, \( \int \frac{\rho_0(r')}{|r - r'|} dr' \) is the Coulomb potential and \( v_{xc}(r) \) is the xc potential. Equation (2.21) is derived in Reference [3].

Inserting Equations (2.21) and (2.22) in (2.20) an expression for the KS potential is obtained.

\[
v_s(r) = v_0(r) + \int \frac{\rho_0(r')}{|r - r'|} dr' + v_{xc}(r) \quad (2.23)
\]

Together, Equations (2.13), (2.14), (2.22) and (2.23) form the KS Equations. The minimum of the exact energy functional (2.7) is found by solving these equations simultaneously.
2.3.2 The exchange correlation potential

In the previous Section the xc potential was defined as the functional derivative of the exchange correlation functional (see Equation (2.22)). There is no explicit expression for the xc potential, since there is no explicit expression available for the xc functional.

In the next Section approximations to the xc functional are presented. With an approximate xc functional the xc potential is approximated. The approximate xc functionals in Section 2.4 depend explicitly on the electron density. The calculation of the approximate xc potential is straightforward.

In Section 2.5 orbital dependent functionals are presented. They do not explicitly depend on the electron density. In the remainder of this Section it is shown that the derivative of orbital dependent functionals exists.

Consider a general orbital and orbital energy dependent functional, $E^{O,DF}_{xc} \{\phi_i, \{\varepsilon_i\}\}$. To obtain an expression for the derivative the chain rule is applied.

$$
\frac{\delta E^{O,DF}_{xc}}{\delta \rho(r)} = v^{DF}_{xc}(r) = \sum_i \int \frac{\delta E^{O,DF}_{xc}}{\delta \phi_i(r''')} \frac{\delta \phi_i(r''')}{\delta \rho(r)} v_s(r') \, dr' \, dr'' + c.c.
+ \sum_i \int \frac{\delta E^{O,DF}_{xc}}{\delta \varepsilon_i} \frac{\delta \varepsilon_i}{\delta v_s(r')} \frac{\delta v_s(r')}{\delta \rho(r)} \, dr' \tag{2.24}
$$

The first term in the integrands is readily evaluated once a particular orbital dependent functional is chosen. The second term is derived from perturbation theory.
2.3. THE KOHN SHAM AND EXCHANGE CORRELATION POTENTIAL

\[
\frac{\delta \phi_i(r'')}{\delta v_s(r')} = -\phi_i(r') G_i(r', r'') \tag{2.25}
\]

\[
\frac{\delta \varepsilon_i}{\delta v_s(r')} = \phi_i^*(r') \phi_i(r') \tag{2.26}
\]

where \( G_i(r'', r') = \sum_j \phi_j^*(r') \phi_j(r'') / (\varepsilon_j - \varepsilon_i) \) is the orbital Green’s function. The last term of the integrands is the inverse of the response function.

\[
\frac{\delta \rho(r)}{\delta v_S(r')} = \chi_s(r, r') = 2 \sum_{i}^{\text{occ}} \sum_{a}^{\text{virt}} \phi_i^*(r) \phi_a(r) \phi_i^*(r') \phi_a(r') \frac{\varepsilon_i - \varepsilon_a}{\varepsilon_i - \varepsilon_a} + \text{c.c.} \tag{2.27}
\]

The xc potential, \( v_{xc}^{\text{ODF}}(r) \), exists if the inverse of the response function, \( \chi_s^{-1}(r, r') \), exists. To prove the existence of the latter, it is shown that the response function has only one singularity associated with a constant potential. The arguments given in Reference [23] are followed. The response function is singular, if there are functions \( \{f(r)\} \) which satisfy

\[
\int \chi_s(r, r') f(r') \, dr' = 0 \tag{2.28}
\]

Multiplication with \( f(r) \) and integrating over \( r \) yields

\[
\int \int f(r) \chi_s(r, r') f(r') \, dr' \, dr = 0 \tag{2.29}
\]

Substituting equation (2.27) into equation (2.29) yields

\[
0 = \sum_{i}^{\text{occ}} \sum_{a}^{\text{virt}} \frac{2}{\varepsilon_i - \varepsilon_a} \int \phi_a(r) \phi_i^*(r) f(r) \, dr \times \int \phi_a^*(r') \phi_i(r') f(r') \, dr' + \text{c.c.} \tag{2.30}
\]
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Since the denominator \((\varepsilon_i - \varepsilon_a)\) is negative and assuming real valued orbitals, it is necessary that

\[
\int \phi_a (r) \phi_i (r) f (r) \, dr = 0 \quad \forall i, \forall a \tag{2.31}
\]

Hence, the response function is singular if \(\phi_i (r) f (r)\) is orthogonal to all virtual orbitals. Rewriting this expression one obtains

\[
\phi_i (r) f (r) = \sum_{j} c_{ij} \phi_j (r) \tag{2.32}
\]

with

\[
c_{ij} = \int \phi_i (r) f (r) \phi_j (r) \, dr \tag{2.33}
\]

The coefficient matrix, \((c)_{ij}\), is symmetric and can be diagonalized with a symmetric matrix, \((u)_{ij}\), and diagonal elements, \(\lambda_i\)

\[
\sum_{i} u_{ki} c_{ij} = \lambda_k u_{kj} \tag{2.34}
\]

Multiplying Equation (2.32) with \(u_{ki}\) and summing over \(i\) it is found that

\[
f (r) \tilde{\phi}_k (r) = \lambda_k \phi_k (r) \tag{2.35}
\]

with

\[
\tilde{\phi}_k (r) = \sum_{i} u_{ki} \phi_i (r) \tag{2.36}
\]

The transformed orbitals \(\tilde{\phi}_k\) in Equation (2.35) are linear combinations of the occupied orbitals. Consequently, they are non-vanishing everywhere except on two-dimensional nodal surfaces. Equation (2.35) can then be divided by \(\tilde{\phi}_k\). This concludes the
2.4. APPROXIMATIONS TO THE EXCHANGE CORRELATION FUNCTIONAL

proof that \( f(r) \) is a constant. Hence, the response function has only one singularity, the constant function. Consequently, the inverse of the response function is uniquely determined up to constant functions.

The derivative of a general orbital and orbital energy dependent functional is calculated from Equation (2.24). The terms entering the expression for the derivative are uniquely determined up to a constant function. Enforcing the potential to go to zero at infinity fixes the constant shift. In conclusion, it has been proven that the derivative of orbital dependent functionals exists.

2.4 Approximations to the Exchange Correlation (XC) Functional

In this Section popular approximations to the xc functional are presented, starting with the local density approximation (LDA) in Section 2.4.1. The LDA was originally formulated by Kohn and Sham [15] and uses the uniform electron gas as a model.

Improving upon the LDA model the gradient of the electron density was introduced. This led to the generalized gradient approximations (GGA). They come in different flavors and are usually named after their inventor(s). Section 2.4.2 gives a list of the most popular GGAs. These include hybrid functionals as well as Meta- and Hyper-GGAs.

2.4.1 The Local Density Approximation (LDA)

The local density approximation (LDA) was the first approximation to the xc functional. In fact, it was already included in the original
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paper by Kohn and Sham [15]. The uniform electron gas is used as a model.

The LDA makes use of the xc energy per particle, $\varepsilon_{xc}(r)$. It is a function of space and gives the xc energy upon integration over the whole space.

$$\int \rho(r) \varepsilon_{xc}(r) dr$$ (2.37)

The xc energy per particle is split up into exchange and correlation. The exchange part can be derived explicitly. It was first derived by Bloch [60] and Dirac [61] and is often referred to as Slater exchange.

$$\varepsilon_x = -\frac{3}{4} \sqrt{\frac{3\rho(r)}{\pi}}$$ (2.38)

There is no explicit expression for the correlation part. Vosko, Wilk and Nusair [62] obtained an analytic expression based on accurate Monte Carlo calculations of the uniform electron gas. The functional is abbreviated with SVWN.

Despite the crude approximation results are good. Structural data for the equilibrium, harmonic frequencies and charge moments are reproduced successfully. However, predicted bond energies are poor.

2.4.2 The Generalized Gradient Approximation (GGA)

Generalized Gradient Approximations include also the gradient of the density in the xc energy per particle, $\varepsilon_{xc}(\rho, \nabla \rho)$. GGAs come in different flavors and include semi-empirical parameters. They are tested against a set of molecules and their thermodynamic prop-
2.5. ORBITAL DEPENDENT FUNCTIONALS

Properties. GGAs give improved bond energies with an error of 5-7 kcal/mol on the test set.

There is a variety of GGAs available. They are usually named after their inventors. The first letter gives the exchange part and the rest specifies the correlation. Popular functionals are BLYP (Becke exchange [63] and Lee-Yang-Parr correlation [64]), BPW86 (Becke exchange [63] and Perdew-Wang correlation [65]) and PW91 (exchange and correlation from Perdew-Wang [66]).

Hybrid Functionals

Inclusion of HF exchange energy improved the performance of GGAs. The most popular hybrid functional is the B3LYP functional. It employs 20% HF exchange and 80% of Becke exchange [63]. The correlation is taken from Lee, Yang and Parr [64]. The amount mixed in HF exchange was determined by fitting on a set of test molecules.

Meta- and Hyper-GGA

Meta-GGAs include the second derivative of the density and the kinetic energy densities $\tau (r) = 0.5 \sum_i^N |\nabla \phi_i (r)|^2$. Examples are the PBE [67] and TPPS [68] functional.

Hyper-GGAs add the exact exchange energy density. The previously mentioned hybrid functionals are simple Hyper-GGAs. A more advanced Hyper-GGA is the TPSS global hybrid [69, 70].

2.5 Orbital Dependent Functionals (ODF)

Orbital Dependent Functionals (ODF) provide the next step in functional development. Kohn Sham (KS) orbitals are the new variables introduced in the functional definition. Three different
types of ODFs have been proposed so far. They are presented in the following Subsection.

For clarity three notations are introduced.

\[
(ij|kl) = \int \frac{\phi_i^*(r_1) \phi_j(r_1) \phi_k^*(r_2) \phi_l(r_2)}{|r_1 - r_2|} dr_1 dr_2 \quad (2.39)
\]

\[
\langle ij|kl \rangle = \int \frac{\phi_i^*(1) \phi_j(1) \phi_k^*(2) \phi_l(2)}{|r_1 - r_2|} d_1 d_2 \quad (2.40)
\]

\[
\langle ij||kl \rangle = (ij|kl) - (ik|jl) \quad (2.41)
\]

Note that the above notations obey the chemists’ convention. The first index pair refers to the orbitals with the first variable and the second index pair refers to the orbitals with the second variable.

The round brackets indicate an integration only over spatial coordinates. The pointy brackets indicate an integration over space and spin.

### 2.5.1 Exact Exchange Functional (EXX)

The simplest ODF is the Exact Exchange Functional (EXX). EXX is, in generaly, the most used ODF. Its energy expression equals the Hartree Fock (HF) energy expression. However, EXX uses KS orbitals instead of HF orbitals.

\[
E_{xc}^{EXX} [\phi_i(r)] = - \frac{1}{2} \sum_i^{occ} \sum_j^{occ} (ij|ij) \quad (2.42)
\]

In Section 2.3.1 we showed that the KS potential is a local multiplicative potential. The optimization problem of finding the minimum energy with the exchange part (2.42) is different from HF. Locality of the potential is an additional constraint compared to
2.5. ORBITAL DEPENDENT FUNCTIONALS

The HF orbitals. The EXX energy is calculated as the expectation value of the single determinant with the EXX orbitals. Therefore, it will be higher than the HF energy.

2.5.2 Perturbation Theory based Functionals

Perturbation theory is a popular tool not only in quantum chemistry. In the KS framework it was first formulated by Görling and Levy [71]. Energy functionals derived from perturbation theory are originally not meant to be used variationally. However, this has been done in the literature [11, 17, 72]. In this Section we present formulas for the second order Görling-Levy perturbation theory (GLPT2) functional. Recent results [11, 73] indicate that the GLPT2 functional is variationally instable for systems with a small gap between highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO). In Reference [74] four functionals are suggested to solve the variational instability by resummation of the perturbation series.

All perturbation theory based xc functionals are decomposed into contributions from exchange, single and double excitations of the KS wave function:

$$E_{xc}^{PT2} = E_{xc}^{EXX} + E_s + E_d$$  \hspace{1cm} (2.43)

In References [11, 74] the contributions from the single excitations are neglected. It has been proven that their contribution is two orders of magnitude smaller than the contributions from the double excitations [72]. The exchange energy is defined as in (2.42).
Second Order Görling-Levy Perturbation Theory (GLPT2)

For the GLPT2 functional the contributions from singles and doubles read:

\[ E_{GLPT2}^{s} = 2 \sum_{i}^{occ} \sum_{a}^{virt} \left| \frac{\langle \phi_{i} | \hat{K} - v_{z(c)} | \phi_{a} \rangle}{\varepsilon_{i} - \varepsilon_{a}} \right|^2 \]  \hspace{1cm} (2.44)

\[ E_{GLPT2}^{d} = \frac{1}{4} \sum_{i,j}^{occ} \sum_{a,b}^{virt} \frac{|\langle ia | jb \rangle|^2}{\varepsilon_{i} + \varepsilon_{j} - \varepsilon_{a} - \varepsilon_{b}} \]  \hspace{1cm} (2.45)

\[ \hat{K} \phi_{a}(r) = \sum_{k}^{occ} \int \frac{\phi_{k}^{*}(r') \phi_{a}(r')}{|r - r'|} \, dr' \phi_{k}(r) \]  \hspace{1cm} (2.46)

The definitions of the xc functional differ slightly in the literature. In Reference [71] only the exchange potential is used in Equation (2.44), whereas Reference [11] employs the full xc potential.

2.5.3 Corrected Hartree functional with \( \varepsilon_{i} \) dependence (CH-\( \varepsilon \))

In this Subsection we introduce a non-perturbative ODF. It has been designed to treat bond dissociation correctly. The formula reads:

\[ E_{xc}^{CH} = -\frac{1}{2} \sum_{ij} w_{i} w_{j} (\phi_{i} \phi_{j} | \phi_{i} \phi_{j}) \]  \hspace{1cm} (2.47)

In the context of Density Matrix Functional Theory (DMFT) functional (2.47) has been obtained by Müller [49] and Buijse and Baerends [50] and has been called Corrected Hartree (CH) by Csanyi and Arias [51]. It employs the natural orbitals (NO) and the orbital weights, \( w_{i} \), are determined with the NO occupations \( n_{i} w_{i} = \sqrt{n_{i}} \).
In the KS approach of DFT an Ansatz for the weights has been formulated. Reference [18] makes the connection with DMFT by choosing \( w_i \) of the form

\[
  w_i = \sqrt{\tilde{n}_i} \tag{2.48}
\]

The \( \tilde{n}_i \) are fictitious occupation numbers of the KS orbitals. In the first application it was chosen to determine the \( \tilde{n}_i \) with the orbital energies \( \varepsilon_i \) using a Fermi type distribution. Hence, we call it the Corrected Hartree-\( \varepsilon \) (CH-\( \varepsilon \)) functional.

\[
  \tilde{n}_i = \frac{2}{1 + \exp\left[\frac{\varepsilon_i - \varepsilon_F}{\tau}\right]} \tag{2.49}
\]

\( \varepsilon_F \) is obtained from the normalization condition \( N = \sum_i \tilde{n}_i \) and \( \tau \) is a two parameter function of the HOMO-LUMO gap \( (\varepsilon_L - \varepsilon_H) \)

\[
  \tau = \sqrt{a (\varepsilon_L - \varepsilon_H) + b (\varepsilon_L - \varepsilon_H)^2} \tag{2.50}
\]

2.6 Optimized Effective Potential (OEP)

The Optimized Effective Potential (OEP) method was formulated by Sharp and Horton [20] and Talman and Shadwick [21]. The OEP is that local multiplicative potential, \( v(\mathbf{r}) \), that yields KS orbitals from the KS Equations (2.13), which minimize a given energy functional, \( E_{ODF} \).

\[
  0 = \frac{\delta E_{ODF}}{\delta v(\mathbf{r})} = \sum_i \int \frac{\delta E_{ODF}^{\delta \phi_i(\mathbf{r}')}}{\delta \phi_i(\mathbf{r}')} \frac{\delta \phi_i(\mathbf{r}')}{\delta v(\mathbf{r})} d\mathbf{r}' + \text{c.c.}
  + \sum_i \frac{\delta E_{ODF}^{\delta \varepsilon_i}}{\delta \varepsilon_i} \frac{\delta \varepsilon_i}{\delta v(\mathbf{r})} \tag{2.51}
\]
The sum runs over all orbitals that enter the energy functional \( E^{ODF} \), which is defined as

\[
E^{ODF} = T_{s} + E_{ext} + E_{coul} + E^{ODF}_{xc}\tag{2.52}
\]

and Equations (2.16), (2.17) and (2.18) for the kinetic, external and Coulomb energy, respectively.

The four derivatives found on the right hand side of equation (2.51) are presented in the following. The derivatives of the energy functional \( E^{ODF} \) are readily evaluated from Equations (2.16), (2.17) and (2.18).

\[
\frac{\delta E^{ODF}}{\delta \phi_i(r')} = n_i \left[ -\frac{1}{2} \nabla^2 + v_{ext}(r') + \frac{1}{2} \int \frac{\rho(r'')}{|r' - r''|} \, dr'' \right] \phi_i^*(r') + \frac{\delta E^{ODF}_{xc}}{\delta \phi_i(r')} \tag{2.53}
\]

\[
\frac{\delta E^{ODF}}{\delta \varepsilon_i} = \frac{\delta E^{ODF}_{xc}}{\delta \varepsilon_i} \tag{2.54}
\]

The second equal sign in Equation (2.53) follows from the KS Equations (2.13) and the KS potential (2.23). Once a particular xc functional is chosen the terms \( \frac{\delta E^{ODF}_{xc}}{\delta \phi_i(r')} \) and \( \frac{\delta E^{ODF}_{xc}}{\delta \varepsilon_i} \) are readily calculated.

From first order perturbation theory the remaining derivatives are found:
2.6. OPTIMIZED EFFECTIVE POTENTIAL

\[
\frac{\delta \phi_i (r')}{\delta v(r)} = - \phi_i (r) G_i (r', r) \quad (2.55)
\]

\[
\frac{\delta \epsilon_i}{\delta v(r)} = \phi_i^* (r) \phi_i (r) \quad (2.56)
\]

\[
G_i (r', r) = \sum_{j, j \neq i} \frac{\phi_j (r) \phi_j^* (r')}{\epsilon_j - \epsilon_i} \quad (2.57)
\]

Inserting Equations (2.53) - (2.57) into equation (2.51) yields

\[
0 = \sum_{i,j,j \neq i} \int \left\{ n_i [\epsilon_i - \nu_{xc}^{ODF} (r')] \phi_j^* (r') + \frac{\delta E_{xc}^{ODF}}{\delta \phi_i (r')} \right\} \phi_j (r') \, dr' \\
\quad \times \frac{\phi_i (r) \phi_j^* (r)}{\epsilon_i - \epsilon_j} + \text{c.c.} + \sum_i \frac{\delta E_{xc}^{ODF}}{\delta \epsilon_i} \phi_i^* (r) \phi_i (r) \quad (2.58)
\]

The above equation can be simplified by realizing that \( \int \epsilon_i \phi_i^* \phi_j = 0 \) for all \( i \neq j \). Introducing the definition \( \nu_{xc}^i (r') = \frac{1}{\phi_i^* (r') \delta \phi_i (r')} \)

and separating \( \nu_{xc} (r') \) yields

\[
\int \chi_s (r', r) \nu_{xc}^{ODF} (r') \, dr' + \text{c.c.} = \sum_{i,j,j \neq i} \frac{\langle \phi_i | \nu_{xc}^i | \phi_j \rangle}{\epsilon_i - \epsilon_j} \phi_i (r) \phi_j^* (r) + \text{c.c.} \\
\quad + \sum_i \frac{\delta E_{xc}^{ODF}}{\delta \epsilon_i} \phi_i^* (r) \phi_i (r) \quad (2.59)
\]

with the response function defined as

\[
\chi_s (r', r) = 2 \sum_{i} \sum_{\alpha} \phi_i^* (r') \phi_\alpha (r') \phi_\alpha^* (r) \phi_i (r) + \text{c.c.} \quad (2.60)
\]
Equation (2.59) is the integral OEP equation. In Section (2.3.2) it was shown that the response function is invertable. Multiplication of (2.59) with $\frac{1}{s}(r; r'; r''; r)$ and integrating over $r$ yields

$$\hat{s}(r_0; r_00) \int s(r; r'; r''; r) \, dr = \sum_{i,j,j \neq i} \int \frac{\langle \phi_i | v_{xc}^i | \phi_j \rangle}{\varepsilon_i - \varepsilon_j} \phi_i(r) \phi_j^*(r) \times \chi_s^{-1}(r, r'') \, dr \, + \, c.c. \nonumber$$

$$+ \sum_i \int \frac{\delta E_{xcODF}^{ODF}}{\delta \varepsilon_i} \phi_i^*(r) \phi_i(r) \chi_s^{-1}(r, r'') \, dr \nonumber$$

(2.61)

where the identity

$$\int \chi_s(r', r) \chi_s^{-1}(r, r'') \, dr = \delta (r' - r'') \nonumber$$

(2.62)

was used.

An explicit equation for the xc potential is obtained from equation (2.61) by performing the integration over $r'$ and relabeling the variables.

$$v_{xcODF}^{ODF}(r) = \sum_{i,j,j \neq i} \int \frac{\langle \phi_i | v_{xc}^i | \phi_j \rangle}{\varepsilon_i - \varepsilon_j} \phi_i(r') \phi_j^*(r') \chi_s^{-1}(r', r) \, dr' + \, c.c. \nonumber$$

$$+ \sum_i \int \frac{\delta E_{xcODF}^{ODF}}{\delta \varepsilon_i} \phi_i^*(r') \phi_i(r') \chi_s^{-1}(r', r) \, dr' \nonumber$$

(2.63)

Different methods of solving this equation numerically [21, 22, 28, 29] or approximately [20, 24, 25, 26, 27] have been proposed. The following Subsections present two different schemes to solve the integral OEP Equations (2.59) using a basis set for the potential.
2.6. OPTIMIZED EFFECTIVE POTENTIAL

2.6.1 The self consistent scheme

Starting from integral OEP Equation (2.59) a self consistent scheme is developed [71, 75, 76]. The xc potential is expanded in a basis.

\[ v_{xc}^{DF}(r) = \sum_p c_p f_p(r) \]  

(2.64)

The integral OEP Equation (2.59) then turns into the matrix Equation

\[ X_s c = t \]

(2.65)

for the vector \( c \) consisting of the expansion coefficients \( c_p \). The response function (Equation (2.60)) is represented by the matrix \( X_s \).

\[ X_{s,pq} = \sum_{i} \sum_{a} \frac{\langle \phi_i | f_p | \phi_a \rangle \langle \phi_a | f_q | \phi_i \rangle}{\varepsilon_i - \varepsilon_a} + c.c. \]

(2.66)

The vector \( t \) represents the right hand side of the integral OEP Equation (2.59). Its elements read

\[
\begin{align*}
    t_p &= \sum_{i,j \neq i} \langle \phi_j | f_p | \phi_i \rangle \frac{\langle \phi_i | v_{xc}^i | \phi_j \rangle}{\varepsilon_i - \varepsilon_j} + c.c \\
    &\quad + \sum_i \frac{\delta E_{zc}^{DF}}{\delta \varepsilon_i} \langle \phi_i | f_p | \phi_i \rangle
\end{align*}
\]

(2.67)

Equations (2.65), (2.66) and (2.67) are solved self consistently. With a guess for the orbitals the vector \( t \) and matrix \( X_s \) are evaluated. Inverting the latter and multiplying with the former a new vector \( c \) is found.
2.6.2 The direct optimization scheme

Starting from Equation (2.51) a direct minimization scheme is derived \[35, 36\]. The electronic potential, sum of Coulomb and xc potential, is decomposed into a reference potential, \(v_0(r)\), and a remainder, which is expanded in a basis.

\[
v_{ee}(r) = v_0(r) + \sum_p c_p f_p(r)
\]  (2.68)

Equation (2.51) transforms to

\[
0 = \frac{\partial E^{ODF}}{\partial c} = \sum_i \int \frac{\delta E^{ODF}}{\delta \phi_i(r')} \frac{\delta \phi_i(r') \partial v(r)}{\partial c_p} dr' dr + c.c.
+ \sum_i \int \frac{\delta E^{ODF}}{\delta \epsilon_i} \frac{\delta \epsilon_i \partial v(r)}{\partial c_p} dr
\]  (2.69)

Using Equations (2.57) and (2.68) and defining

\[
v_{ODF}^i(r) = \frac{1}{\phi_i^*(r) \delta \phi_i(r)}
\]  (2.70)

yields

\[
0 = \frac{\partial E^{ODF}}{\partial c} = \sum_{i,j,i\neq j} \langle \phi_j | f_p | \phi_i \rangle \frac{\langle \phi_i | v_{ODF}^i | \phi_j \rangle}{\epsilon_i - \epsilon_j} + c.c
+ \sum_i \frac{\delta E^{ODF}}{\delta \epsilon_i} \langle \phi_i | f_p | \phi_i \rangle
\]  (2.71)

Note the difference between Equations (2.67) and (2.71). The former includes the matrix element of \(v_{xc}^i(r)\), i.e. the xc part of the ODF. The latter includes the matrix element of \(v_{ODF}^i(r)\), i.e. all parts of the ODF.

Equation (2.71) presents the gradient of an ODF. Furnishing an optimization routine with the gradient yields the energy minimum.
Consequences of Vanishing HOMO-LUMO Gap

In this Chapter consequences of a vanishing highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO) gap are shown for the Görling-Levy second order perturbation theory functional (GLPT2 in Section (2.5.2)) and the Corrected Hartree functional with $\epsilon_i$ dependence (CH-$\epsilon$ Section (2.5.3)). In Section 3.1 it is demonstrated that when the local Kohn-Sham (KS) potential is approximated by an expansion in a set of basis functions, exact degeneracy of HOMO and LUMO can occur, if a finite orbital basis set is used. Two numerical examples for the He atom are given. In Section 3.2 the variational collapse of the Görling-Levy second order perturbation theory (GLPT2) functional from Section 2.5.2 is shown. This is demonstrated for the He atom, which until now stood out as a “safe” simple case [11]. In Section 3.3 the variational breakdown of the Corrected Hartree functional with $\epsilon_i$ dependence from Section 2.5.3 is shown, when the HOMO-LUMO gap is used to regulate the contribution of virtual orbitals.
CHAPTER 3. CONSEQUENCES OF VANISHING HOMO-LUMO GAP

3.1 KS Potentials with Vanishing HOMO-LUMO Gap

The KS potential \( v_s(r) \) is constructed according to Section 2.6.2 as the sum of external potential \( v_{\text{ext}}(r) \), a fixed reference potential \( v_0(r) \) and a linear combination of the expansion functions \( f_p(r) \).

\[
v_s(r) = v_{\text{ext}}(r) + v_0(r) + \sum_{p}^{M} c_p f_p(r)
\]  

(3.1)

It has recently been stressed [40] that the \( M \) coefficients in an expansion of the potential in a set of \( M \) basis functions could be determined from a set of conditions. In reference [77] it is pointed out that this is only true if the products of the occupied orbitals with the unoccupied orbitals are linearly independent. If this is the case, one can e.g. put the matrix elements that couple the occupied and unoccupied Hartree-Fock orbitals to zero. With the local potential fixed in this way, the full KS matrix may be obtained and diagonalized, leading to orbitals which are only a linear transformation of the HF occupied orbitals, and will therefore yield an EXX energy equal to the HF energy in the same basis set. With more expansion functions for the potential one may apply more conditions, which opens the way to manipulate only a given orbital energy. In particular, suppose for instance the HOMO and LUMO of He are decoupled from all other orbitals by choosing

\[
\left\langle \phi_i^{HF} \left| v_{xc}(r) \right| \phi_j^{HF} \right\rangle = -\left\langle \phi_i^{HF} \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) + v_H(r) \right| \phi_j^{HF} \right\rangle
\]  

(3.2)

for \( i = 1,2 \) and \( j \neq i \) running over all orbitals. Then, introducing the conditions
\[ \langle \phi_i^{HF} | v_{xc}(r) | \phi_i^{HF} \rangle = c - \langle \phi_i^{HF} \frac{1}{2} \nabla^2 + v_{ext}(r) + \psi_H(r) | \phi_i^{HF} \rangle \]

(3.3)

for both HOMO and LUMO, would fix the HOMO and LUMO orbital energies at the same degenerate value \( c \). Although this is a somewhat artificial construction, the example does demonstrate that in a finite orbital basis (with a limited number of KS matrix elements), degeneracy of HOMO and LUMO can occur with a sufficiently flexible potential expansion.

As has been noticed before [23], it may not be possible to obtain exact degeneracy in a local potential with an exact (e.g. basis set free, numerical) solution for the orbitals. It does not exclude near-degeneracy in the exact solution, however, We believe that it should be possible to close the HOMO-LUMO gap to arbitrarily small values in accurate numerical solutions.

Our results, which are presented in the remainder of this Section and which feature (near-) degeneracy of HOMO and LUMO orbital energies, were not “constructed” by using a judicious set of linear equations to enforce the HOMO-LUMO degeneracy as indicated above. Rather they were found in regular optimization calculations, where one tries to optimize the potential expansion coefficients (see tables 3.1 and 3.2).

The direct optimization scheme from Section 2.6.2 is implemented in a new program. It is written in Python [78] using routines from the Scipy [79] and PyQuante [80] packages. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimizer of the Scipy package is used to find the energy minimum. The gradient is calculated from the condition (2.69), so that the optimization turns to the minimization of the derivatives of the total energy with respect to the \( \beta \).

As basis set for the He atom we use an uncontracted cc-pVTZ
basis set of Gaussian type orbitals [81, 82]. The Fermi-Amaldi potential

\[ v_0(r) = \frac{N - 1}{N} \int \frac{\rho_0(r')}{|r - r'|} dr' \]  

(3.4)

is chosen as the reference potential \( v_0(r) \) in Equation (2.68), with \( \rho_0(r) \) being the density of the lowest solution of the one-electron Hamiltonian \( \hat{H} = \sum_{i=1}^{2} \left\{ -\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(r_i) \right\} \) for the He atom. A set of \( M \) even-tempered primitive Gaussian s-functions with exponents \( \alpha_i \) with \( \alpha_i = \alpha_0 (\alpha_{M-1}/\alpha_0)^{i/(M-1)} \) for \( 0 \leq i \leq M - 1 \) are chosen as the potential expansion functions \( f_p \), cf. tables 3.1 and 3.2.

We have performed calculations with various potential basis sets. All of them converged to a point with gradient elements less than \( 10^{-5} \). However, not all of the minima obtained exhibit a near-degeneracy of HOMO and LUMO. In fact, the calculation with the second potential basis of table 3.2 has produced, initially, a local minimum with non-degenerate HOMO-LUMO. Distortion of this initial solution and subsequent optimization led to the result presented here. That one may indeed easily get trapped in a local minimum in these optimizations, is also apparent from the fact that we found the collapse only in optimizations with a larger number of expansion functions for the potentials (i.e. 20) than the minimum number needed for the artificial construction of HOMO-LUMO degeneracy, see above. Apparently, our optimizations with smaller numbers of potential expansion functions (but equal to or larger than the minimum number) have only reached local minima.

Radial plots of two different potentials \( v_s(r) \) constructed for the He atom are displayed in figure 3.1. Figure 3.2 shows the respective 1s HOMOs and figure 3.3 shows the respective 2s LUMOs. Both potentials are constructed with 20 functions \( f_p(r) \) and the corresponding exponents and the expansion coefficients are presented.
### 3.1. KS POTENTIALS WITH VANISHING HOMO-LUMO GAP

**Table 3.1:** The exponents $\alpha$ and the coefficients $c_p$ for potential I of the He atom

<table>
<thead>
<tr>
<th>$p$</th>
<th>Exponents</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>400000.00</td>
<td>20.34290012</td>
</tr>
<tr>
<td>1</td>
<td>202868.55</td>
<td>-24.79974276</td>
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<tr>
<td>2</td>
<td>102889.12</td>
<td>-18.43015069</td>
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<tr>
<td>3</td>
<td>52182.42</td>
<td>-4.72107194</td>
</tr>
<tr>
<td>4</td>
<td>26465.43</td>
<td>-5.83199565</td>
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<tr>
<td>5</td>
<td>13422.51</td>
<td>-27.31011334</td>
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<td>6</td>
<td>6807.51</td>
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<td>7</td>
<td>3452.58</td>
<td>-10.38149182</td>
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<td>8</td>
<td>1751.05</td>
<td>-11.40181584</td>
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<tr>
<td>9</td>
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<td>10</td>
<td>450.41</td>
<td>-1.05218907</td>
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<tr>
<td>11</td>
<td>228.43</td>
<td>14.28680689</td>
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<tr>
<td>12</td>
<td>115.86</td>
<td>31.20829688</td>
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<td>13</td>
<td>58.76</td>
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<tr>
<td>15</td>
<td>15.11</td>
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<tr>
<td>19</td>
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</tr>
</tbody>
</table>
### CHAPTER 3. CONSEQUENCES OF VANISHING HOMO-LUMO GAP

#### Table 3.2: The exponents $\alpha$ and the coefficients $c_p$ for potential $\text{II}$ of the He atom

<table>
<thead>
<tr>
<th>$p$</th>
<th>Exponents</th>
<th>Coefficients</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>400000.00</td>
<td>19.96085707</td>
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<td>1</td>
<td>168679.85</td>
<td>-25.47969081</td>
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<tr>
<td>2</td>
<td>71132.23</td>
<td>-19.75686011</td>
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<td>3</td>
<td>29996.44</td>
<td>-6.99267269</td>
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<td>4</td>
<td>12649.49</td>
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<tr>
<td>5</td>
<td>5334.28</td>
<td>-33.33814436</td>
</tr>
<tr>
<td>6</td>
<td>2249.47</td>
<td>-21.19876441</td>
</tr>
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<td>7</td>
<td>948.60</td>
<td>-7.87291680</td>
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<td>8</td>
<td>400.02</td>
<td>9.29487185</td>
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<td>9</td>
<td>168.69</td>
<td>25.14313628</td>
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<td>12.65</td>
<td>1.82776574</td>
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<td>5.33</td>
<td>25.39100154</td>
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<td>2.25</td>
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<tr>
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<td>0.17</td>
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<tr>
<td>18</td>
<td>0.07</td>
<td>83.95434867</td>
</tr>
<tr>
<td>19</td>
<td>0.03</td>
<td>-42.48759091</td>
</tr>
</tbody>
</table>
3.1. KS POTENTIALS WITH VANISHING HOMO-LUMO GAP

for each potential in tables 3.1 and 3.2, respectively. As one can see from figure 3.1, the potentials are distinctly different from each other, but they both yield nearly perfectly degenerate HOMO and LUMO, with the corresponding differences \((\varepsilon_H - \varepsilon_L)\) being only 0.000005 and 0.000004 Hartree, respectively (see table 3.3). Both potentials vanish with the distance from the He nucleus, though potential II does this much more slowly due to the inclusion of more diffuse expansion functions \(f_p(r)\) in the latter case (see table 3.2). In the inner region both potentials display strong oscillations as can be inferred from the large and sign changing expansion coefficients (see tables 3.1 and 3.2). Both, the strong oscillations and the two distinctly different potentials yielding the same energy, are in line with previous findings in the literature [40].

The degenerate HOMO and LUMO orbitals show very different forms compared to “normal” orbitals. Figures 3.2 and 3.3 plot the electron density along the radius. The 1s AO from potential I shows a shoulder around 0.1 Bohr (dotted curve in figure 3.2). It originates from the peak of potential I at the same distance (see figure 3.1). Potential II exhibits a more pronounced peak at this distance (see figure 3.1). Consequently, the 1s AO from potential II exhibits a minimum around 0.1 Bohr (solid curve in figure 3.2). The 1s AOs from both potentials extend to about 1 Bohr. This is the normal radius of a 1s AO, which can be deferred from the 1s HF orbital shown for comparison (dashed curve in figure 3.2).

The shape of the LUMO is very different from that of a typical 2s AO. Indeed, both LUMOs have a large peak at the nucleus. The amplitudes are much larger than that of the 1s AOs. The 2s AOs are completely confined to the near-nuclear region (see figure 3.3). They only extend up to 0.2 Bohr away from the nucleus. Hence, they are completely caught in the steep minimum of the potential near the nucleus (see figure 3.1). Both 2s AOs do not extend beyond
CHAPTER 3. CONSEQUENCES OF VANISHING HOMO-LUMO GAP

Figure 3.1: Potentials I and II

The full Kohn-Sham potential (including the nuclear attraction potential) in Hartree units for the potentials I and II of tables 3.1 and 3.2.
Figure 3.2: HOMOs for potentials I and II

The HOMOs of He are plotted in units of electron/Bohr$^3$ for the potentials I and II of tables 3.1 and 3.2, as well as the HF HOMO.
The LUMOs of He are plotted in units of electron/Bohr$^3$ for the potentials I and II of tables 3.1 and 3.2.

the maximum of the respective potentials, located around 0.2 Bohr. Due to this peculiar form of the 2s LUMOs, their kinetic energy is many times larger than that for the 1s AOs.

In table 3.3 we display a few contributions

$$\langle 2s | \hat{\Omega} | 2s \rangle - \langle 1s | \hat{\Omega} | 1s \rangle$$

(3.5)

to the (vanishing) HOMO-LUMO gap $\varepsilon_{2s} - \varepsilon_{1s}$. The kinetic energy contribution with $\hat{\Omega} = -\frac{1}{2} \nabla^2$ of more than 800 Hartree in table 3.3 demonstrates the extremely high kinetic energy of 2s. However, the contribution from the electronic potential ($\hat{\Omega} = v_0 (r) + \sum_p c_p f_p (r)$)
3.2. COLLAPSE OF THE GÖRLING-LEVY SECOND-ORDER PERTURBATION THEORY FUNCTIONAL

Table 3.3: The HOMO-LUMO gap and its various components \( \langle 2s | \hat{\Omega} | 2s \rangle - \langle 1s | \hat{\Omega} | 1s \rangle \) for the potentials I and II

<table>
<thead>
<tr>
<th></th>
<th>Potential I</th>
<th>Potential II</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO-LUMO gap</td>
<td>0.000005</td>
<td>0.000004</td>
</tr>
<tr>
<td>Kinetic component</td>
<td>818.524227</td>
<td>880.384443</td>
</tr>
<tr>
<td>Nuclear-attraction component</td>
<td>-88.523870</td>
<td>-87.630648</td>
</tr>
<tr>
<td>Electron-electron component</td>
<td>-730.000352</td>
<td>-792.753791</td>
</tr>
</tbody>
</table>

Kinetic: \( \hat{\Omega} = \frac{1}{2} \nabla^2 \); Nuclear attraction: \( \hat{\Omega} = -2/r \); Electron-electron interaction: \( \hat{\Omega} = v_0 (r) + \sum_p c_p f_p (r) \). All energies are in Hartree.

It has an exceedingly large negative value (see table 3.3). The contributions of these two components (kinetic and electronic potential) to the orbital energy difference add up to a substantial positive value, which, however, is virtually perfectly canceled by the very large negative nuclear-attraction energy contribution, thus producing a 2s orbital energy which is virtually identical to that of the 1s. The large negative nuclear-attraction energy contribution implies that the nuclear attraction energy for the 2s is much larger (negative) than the one for the 1s, doubtless because of the large near-nuclear peak of the 2s.

3.2 Collapse of the Görling-Levy Second-Order Perturbation Theory (GLPT2) Functional

It is well known that the GLPT2 energy (see Section 2.5.2) is not bound from below and GLPT2 breaks down when the gap \( (\varepsilon_a - \varepsilon_z) \)
between the occupied and virtual orbitals becomes too low, because $E_{xc}^{PT2}$ includes $(\varepsilon_a - \varepsilon_i)$ in its denominators. In the two-electron case considered in this Chapter the components of the GLPT2 energy are reduced to

$$E_{xc}^{PT2} = E_x + E_s^{(2)} + E_d^{(2)}$$

(3.6)

$$E_x = -\frac{1}{2} \langle \phi_H \phi_H | \phi_H \phi_H \rangle$$

(3.7)

$$E_s^{(2)} = 2 \sum_{a > H} \frac{\langle \phi_H | v_c(r) | \phi_a \rangle^2}{\varepsilon_H - \varepsilon_a}$$

(3.8)

$$E_d^{(2)} = \sum_{ab > H} \frac{\langle \phi_H \phi_H | \phi_a \phi_b \rangle^2}{2\varepsilon_H - \varepsilon_a - \varepsilon_b}$$

(3.9)

where $v_c(r) = v_{x(c)}(r) - v_x(r)$. Note that when self-consistent EXX orbitals are used in GLPT2 [71], the term (3.8) vanishes since $v_c(r) = 0$, so that the xc energy is reduced to the sum of (3.7) and (3.9).

Inserting the orbitals $\{\phi_i(r)\}$ and the orbital energies $\{\varepsilon_i\}$ of the potentials I and II (see tables 3.1 and 3.2) presented in the previous Section in the energy expressions (3.6) of perturbation theory, one obtains nearly divergent terms in both the second-order single-excitation energy $E_s^{(2)}$, and the double-excitation energy $E_d^{(2)}$. In the former case this will be the term (3.8) with vanishing difference $(\varepsilon_L - \varepsilon_H)$ in its denominator, while in the latter case term (3.9) with twice the difference $(\varepsilon_L - \varepsilon_H)$ in the denominator nearly diverges. With this near divergence, the GLPT2 energy of the He atom tends to minus infinity, so that the potentials $v_s(r)$ presented in this Section prove that variational collapse occurs, regardless of the question whether a potential with numerically even more precise HOMO-LUMO degeneracy could be found by further optimization of the potential with for instance more expansion functions, and
3.3. BREAKDOWN OF THE CORRECTED HARTREE FUNCTIONAL WITH $\varepsilon_i$ DEPENDENCE

irrespective of how these potentials have been found. (The ones displayed in tables 3.1 and 3.2 and figure 3.1 actually have been obtained in an optimization described in the next Section). So collapse of the GLPT2 energy will occur with the OEP method whether only the second-order energy $E_d^{(2)}$ is retained, or the additional contribution $E_s^{(2)}$ is taken into account [11]

3.3 Breakdown of the Corrected Hartree Functional with $\varepsilon_i$ dependence (CH-$\varepsilon$)

In Section 3.1 we stress that the problem of the perturbation theory functional is its dependence on the HOMO-LUMO energy difference in the denominator. This, as is well known, makes such a functional unsuitable in cases of molecular dissociation, where the HOMO-LUMO degeneracy will always occur. We have been investigating non-perturbative orbital-dependent xc functionals which, in particular, are designed to treat the situation of weak bonding (dissociation) correctly. The simplest functional of this type has the following form

$$E_{xc}^{ODF} = -\frac{1}{2} \sum_{ij} w_i w_j (\phi_i \phi_j | \phi_i \phi_j)$$

where the sum over $i$ and $j$ may run to infinity.

Note, that in the context of density matrix functional theory (DMFT, see Chapter 6) the functional (3.10) of the natural orbitals (NOs) and orbital weights $w_i$ determined with the NO occupations $n_i$, $w_i = \sqrt{n_i}$, was already obtained by Müller [49] and by Buijse and Baerends [50], and has been called the Corrected Hartree (CH) functional by Csanyi and Arias [51]. Applying (3.10) within the KS approach of DFT, we have used for $w_i$ an Ansatz [18] where the connection with DFT was made by choosing $w_i$ in the form
CHAPTER 3. CONSEQUENCES OF VANISHING HOMO-LUMO GAP

\[ w_i = \sqrt{\bar{n}_i} \] (3.11)

where \( \bar{n}_i \) are fictitious occupation numbers of the KS orbitals. In that first application we have chosen to determine the \( \bar{n}_i \) with the orbital energies \( \varepsilon_i \) from a Fermi type distribution

\[ \bar{n}_i = \frac{2}{1 + \exp \left[ \frac{\varepsilon_i - \varepsilon_F}{\tau} \right]} \] (3.12)

where \( \varepsilon_F \) is obtained from the normalization condition \( \sum_i \bar{n}_i = N \) and \( \tau \) is a two-parameter function of the HOMO-LUMO gap \( (\varepsilon_L - \varepsilon_H) \)

\[ \tau = \sqrt{a (\varepsilon_L - \varepsilon_H) + b (\varepsilon_L - \varepsilon_H)^2} \] (3.13)

The functional (3.10) with Ansatz (3.11), (3.12) and (3.13) has been applied to the calculation of the potential curve of the hydrogen molecule \( \text{H}_2 \) [18] using the common energy denominator approximation (CEDA) [19, 25] to obtain the potential. In the dissociation limit the HOMO and LUMO become degenerate and then their weights in (3.10) become equal. This is desired in this case, since HOMO and LUMO should contribute equally to the functional (3.10) at that point [83]. In principle, however, such a form of the \( w_i \) parameters opens the possibility that also in cases where HOMO-LUMO degeneracy should not occur, the OEP procedure tries to obtain such a shape of the potential \( v_s (r) \) that this degeneracy does occur, and the LUMO becomes strongly involved in the xc energy expression. This will happen if we make the OEP potential search sufficiently flexible and thus lower the energy. The two potentials documented in the previous Section were actually found this way. Indeed, the flexible form (3.1) of the OEP potential and
the flexible set of the potential expansion functions presented in tables 3.1 and 3.2 allows to construct OEP potentials with virtually degenerate HOMO and LUMO (see table 3.3).

Table 3.4 presents the fictitious HOMO $\tilde{n}_H$ and LUMO $\tilde{n}_L$ occupations as well as the resultant total energies corresponding to the functional (3.10) and a number of energy components for both potentials considered in the previous Section. Due to the above mentioned HOMO-LUMO degeneracy, $\tilde{n}_H$ and $\tilde{n}_L$ are both very close to 1, which means strong involvement of the LUMO in the xc energy expression (3.10). This produces unphysically low xc energies and, as a result extremely low total energies, which in both cases are below -9 Hartree (see table 3.4; the full CI total energy is -2.90813 H). The reason for these low energies is the above mentioned semi-core form of $\phi_L$ (see figure 3.1) with a large integral $(\phi_L \phi_L|\phi_L \phi_L)$, which together with the weight $w_L \approx 1$ produces a very low contribution $-\frac{1}{2} w_L^2 (\phi_L \phi_L|\phi_L \phi_L)$ to the xc energy (3.10), which is not compensated by a similar term in the Hartree energy,

$$W_H = -\frac{1}{2} \int \frac{\rho(r')}{|r-r'|} d\rho d\rho'$$

since only occupied orbitals enter the density. Thus, the OEP potentials $v_s(r)$ documented in the previous Section produce not only variational collapse of GLPT2, but also breakdown of the Ansatz (3.12) for the determination of the weights of the virtual orbitals in the energy (3.10).

3.4 Conclusions

In this Chapter two local potentials $v_s(r)$ are constructed for the He atom, which, in a finite orbital basis, have almost perfectly degenerate highest occupied and lowest unoccupied AOs. The vanishing HOMO-LUMO gap leads to the total collapse of the variational second-order perturbation theory GLPT2 and to a breakdown of
Table 3.4: The total energies, energy contributions and fictitious occupations for the He atom using the Corrected Hartree (CH) functional

<table>
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<tr>
<th></th>
<th>Potential I</th>
<th>Potential II</th>
</tr>
</thead>
<tbody>
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<td>Total energy</td>
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</tr>
<tr>
<td>Kinetic energy</td>
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<tr>
<td>Nuclear-attraction energy</td>
<td>-5.508031</td>
<td>-7.225226</td>
</tr>
<tr>
<td>Hartree energy</td>
<td>1.593366</td>
<td>2.367731</td>
</tr>
<tr>
<td>XC energy</td>
<td>-7.898873</td>
<td>-8.116148</td>
</tr>
<tr>
<td>$\tilde{n}_H$</td>
<td>1.00951</td>
<td>1.00698</td>
</tr>
<tr>
<td>$\tilde{n}_L$</td>
<td>0.99050</td>
<td>0.99302</td>
</tr>
</tbody>
</table>

All energies are in Hartree. The full CI total energy is -2.90813 H.
the total energy expression of the non-perturbative virtual orbital dependent functional (3.10) if the involvement of the virtual orbitals is regulated with a Fermi type distribution of the fictitious occupation number, Equations (3.11) and (3.12).

The HOMO-LUMO degeneracy is not an accidental or spurious result. We have demonstrated the existence of distinctly different potentials with virtually the same HOMO-LUMO degeneracy, and have indicated that this phenomenon is understandable in the case of finite orbital basis sets. Rather, the stable GLPT2 solutions reported in the literature [11] are spurious. The potentials yielding collapse have apparently not been found, possibly by a too restricted expansion basis, or because the optimization got locked in a local minimum. Since we obtain the energy collapse for the case of He, which until now stood out as a “safe” case, it is likely that the systems that already showed signs of variational instability with restricted searches over the space of potentials will exhibit total collapse if optimization of the potentials is carried out to a sufficient degree of variational freedom.

The present results also highlight the problems, which are faced by the development of DFT xc functionals of the “fifth” generation with virtual KS orbitals. One can see from the general KS expressions (2.15) and (2.14), that virtual orbitals enter only the xc energy, while other components of the total energy depend only on the occupied orbitals. In this case, the OEP energy optimization (2.51) might well produce virtual orbitals of a bizarre form if the xc energy and, as a result, the total energy are lowered in this way. Such bizarre orbitals might have a very high kinetic energy, as in the present case of the 2s LUMO of He. However, this latter feature would have no effect on the energy, since the KS kinetic energy $T_S$ involves only occupied orbitals. With this, the OEP optimization may lead to an unphysically low energy or even to total variational
A safer way to use xc functionals with virtual orbitals is a non-variational approach, which can be applied to perturbational and non-perturbative functionals. In this case, in order to calculate the orbitals and orbital energies, one can use exchange-only EXX, as in the above mentioned non-variational GLPT2 [84, 85, 86]. At the higher, correlated level one can employ the potentials designed especially to produce reliable occupied and virtual orbitals and orbital energies, such as that with the statistical averaging of (different) orbitals potentials (SAOP) [87] or the potential with gradient-regulated asymptotic connection (GRAC) [88].
4

Precision of Total Energy and Orbital Energy

In this Chapter the precision of the total energy and the orbital energies with the direct optimization method (Section 2.6.2) is assessed. The EXX functional from Section 2.5.1 is used as a test case. The interdependence of the basis sets for the orbitals and potential is investigated. The effect of the reference potential is analyzed.

4.1 Method and Computational details

As described in Section 2.6.2 the electronic potential is decomposed in a reference potential $v_0(r)$ and a linear combination of M Gaussian functions, $\{f_p(r)\}$

$$v_{ee}(r) = v_0(r) + \sum_{p}^M f_p(r) \quad (4.1)$$

The direct optimization scheme of Section 2.6.2 is applied to solve the OEP Equation (2.51). The gradient for the EXX functional is calculated from Equation (2.71):

$$0 = \frac{\partial E^{EXX}}{\partial c_p} = 2 \sum_{\tau} \sum_{a>H} \langle \phi_\tau | f | \phi_a \rangle \frac{\langle \phi_a | f_p | \phi_\tau \rangle}{\varepsilon_\tau - \varepsilon_a} \quad (4.2)$$
where \( \hat{f} \) is the Fock operator evaluated with \( \{ \phi_i \} \)

\[
\hat{f}\phi_a (r) = \left\{ -\frac{1}{2} \nabla^2 + v_{\text{ext}} (r) + \int \frac{\rho(r')}{|r - r'|} dr' \right\} \phi_a (r) \\
- \sum_j \phi_j (r) \int \frac{\phi_j^*(r') \phi_a (r')}{|r - r'|} dr'
\] (4.3)

As an addition to this scheme, one can impose, in order to refine the calculated orbital energies \( \varepsilon_i \), an exact condition for EXX. In Reference [24] it is shown that

\[
\varepsilon_H = \langle \phi_H \left| -\frac{1}{2} \nabla^2 + v_s (r) \right| \phi_H \rangle = \langle \phi_H \left| \hat{f} \right| \phi_H \rangle = \langle \hat{f} \phi_H | \phi_H \rangle
\] (4.4)

where the local potential \( v_s (r) \) is the sum of the external potential \( v_{\text{ext}} (r) \) and the electronic potential of equation (4.1).

To solve Equation (4.2) with the additional constraint Equation (4.4), a penalty function procedure is employed. Within this procedure the augmented functional

\[
L = E^{\text{EXX}} + \lambda \Delta^2
\] (4.5)

is minimized for a certain value of \( \lambda \), where

\[
\Delta = \langle \phi_H \left| \hat{f} \right| \phi_H \rangle - \varepsilon_H
\] (4.6)

The gradient for the constraint optimization is

\[
\frac{\partial L}{\partial c_p} = \frac{\partial E^{\text{EXX}}}{\partial c_p} + 2 \lambda \Delta \frac{\partial \Delta}{\partial c_p} = 0
\] (4.7)

The derivative of the second term of \( \Delta \) is readily calculated from equations (4.4) and (4.1).

\[
\frac{\partial \varepsilon_H}{\partial c_p} = \langle \phi_H \left| f_p \right| \phi_H \rangle
\] (4.8)
4.1. METHOD AND COMPUTATIONAL DETAILS

The derivative of first term of $\Delta$ is obtained by the chain rule

$$
\frac{\delta \langle \phi_H | \hat{f} | \phi_H \rangle}{\delta c_p} = \sum_j \int \int \frac{\delta \langle \phi_H | \hat{f} | \phi_H \rangle}{\delta \phi_j(r)} \frac{\delta \phi_j(r)}{\delta v_s(r')} \frac{\partial v_s(r')}{\partial c_p} + c.c. \quad (4.9)
$$

The second factor of the right hand side of equation (4.9) is derived from perturbation theory to be

$$
\frac{\delta \phi_j(r)}{\delta v_s(r')} = - \phi_j(r') G_j(r, r') \quad (4.10)
$$

$$
G_j(r, r') = \sum_{k \neq j} \frac{\phi_k^*(r') \phi_k(r)}{\varepsilon_k - \varepsilon_j} \quad (4.11)
$$

The third factor of the right hand side of equation (4.9) is readily calculated from equations (4.4) and (4.1).

$$
\frac{\partial v_s(r')}{\partial c_p} = f_p(r') \quad (4.12)
$$

To derive the first factor of the right hand side of equation (4.9) the numerator is given explicitly.

$$
\langle \phi_H | \hat{f} | \phi_H \rangle = T + J + K \quad (4.13)
$$

$$
T = \int \phi_H^*(r) \left[ -\frac{1}{2} \nabla^2 + v_{ext}(r) \right] \phi_H(r) \, dr \quad (4.14)
$$

$$
J = + 2 \sum_i \int \int \frac{\phi_H^*(r_1) \phi_H(r_1) \phi_i^*(r_2) \phi_i(r_2)}{r_{12}} \, dr_1 \, dr_2 \quad (4.15)
$$

$$
K = - \sum_i \int \int \frac{\phi_H^*(r_1) \phi_i(r_1) \phi_i^*(r_2) \phi_H(r_2)}{r_{12}} \, dr_1 \, dr_2 \quad (4.16)
$$
CHAPTER 4. PRECISION OF TOTAL ENERGY AND ORBITAL ENERGY

The derivative of the three components with respect to orbital \( j \) are

\[
\frac{\delta T}{\delta \phi_j(r)} = \delta_{jH} \phi^*_H(r) \left[ -\frac{1}{2} \nabla^2 + v_{ext}(r) \right] \tag{4.17}
\]

\[
\frac{\delta J}{\delta \phi_j(r)} = 2 \int \frac{\phi^*_H(r_1) \phi_H(r_1) \phi^*_j(r_2)}{r_{12}} dr_1 \\
+ \delta_{Hj} 2 \sum_{i}^{\text{occ}} \int \frac{\phi^*_H(r_1) \phi^*_i(r_2) \phi_i(r_2)}{r_{12}} dr_2 \tag{4.18}
\]

\[
\frac{\delta K}{\delta \phi_j(r)} = - \int \frac{\phi^*_H(r_1) \phi^*_j(r_2) \phi_H(r_2)}{r_{12}} dr_2 \\
- \delta_{Hj} \sum_{i}^{\text{occ}} \int \frac{\phi_H(r_1) \phi_i(r_1) \phi^*_i(r_2)}{r_{12}} dr_1 \tag{4.19}
\]

Inserting equations (4.10) - (4.19) in equation (4.9) yields the derivative of first factor of the right hand side of equation (4.9) with respect to the expansion coefficient \( p \).
\[
\frac{\delta \langle \phi_H | f | \phi_H \rangle}{\delta c_p} = - \sum_{j}^{occ} \int \int \delta_{jH} \phi^{*}_H (r) \left[ -\frac{1}{2} \nabla^2 + v_{ext} (r) \right] \\
\times \phi_j (r') G_j (r, r') f_p (r') \, dr \, dr' \\
- 2 \sum_{j}^{occ} \int \int \int \frac{\phi^{*}_H (r_1) \phi_H (r_1) \phi^{*}_j (r_2)}{r_{12}} \, dr_1 \\
\times \phi_j (r') G_j (r_2, r') f_p (r') \, dr_2 \, dr' \\
- \delta_{Hj} 2 \sum_{j}^{occ} \int \int \sum_{i}^{occ} \int \frac{\phi^{*}_H (r_1) \phi^{*}_i (r_2) \phi_i (r_2)}{r_{12}} \, dr_2 \\
\times \phi_j (r') G_j (r_1, r') f_p (r') \, dr_1 \, dr' \\
+ \sum_{j}^{occ} \int \int \int \frac{\phi^{*}_H (r_1) \phi^{*}_j (r_2) \phi_H (r_2)}{r_{12}} \, dr_2 \\
\times \phi_j (r') G_j (r_1, r') f_p (r') \, dr_1 \, dr' \\
+ \delta_{Hj} \sum_{j}^{occ} \int \int \sum_{i}^{occ} \int \frac{\phi^{*}_H (r_1) \phi_i (r_1) \phi^{*}_j (r_2)}{r_{12}} \, dr_2 \\
\times \phi_j (r') G_j (r_2, r') f_p (r') \, dr_2 \, dr' + c.c. \quad (4.20)
\]

Inserting the definition for the Green’s function (4.11) and performing the integration we obtain
\[
\frac{\delta \langle \phi_H | \hat{f} | \phi_H \rangle}{\delta c_p} = - \sum_{k \neq H}^{\text{occ}} \left\langle \phi_H | \left( -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) \right) \phi_k \right\rangle \frac{\langle \phi_k | f_p | \phi_H \rangle}{\epsilon_k - \epsilon_H} \\
- 2 \sum_{j \neq k}^{\text{occ}} \langle \phi_H \phi_H | \phi_j \phi_k \rangle \frac{\langle \phi_k | f_p | \phi_j \rangle}{\epsilon_k - \epsilon_j} \\
- 2 \sum_{i \neq k \neq H}^{\text{occ}} \langle \phi_H \phi_k | \phi_i \phi_i \rangle \frac{\langle \phi_k | f_p | \phi_H \rangle}{\epsilon_k - \epsilon_H} \\
+ \sum_{j \neq k}^{\text{occ}} \langle \phi_H \phi_H | \phi_j \phi_H \rangle \frac{\langle \phi_k | f_p | \phi_j \rangle}{\epsilon_k - \epsilon_j} \\
+ \sum_{i \neq k \neq H}^{\text{occ}} \langle \phi_H \phi_i | \phi_i \phi_k \rangle \frac{\langle \phi_k | f_p | \phi_H \rangle}{\epsilon_k - \epsilon_H} + \text{c.c.} \tag{4.21}
\]

We note that in the first term of the above equation we can extend the sum to run over all orbitals except H, since we add only zero elements. Then the first, the third and the fifth term add up to matrix elements of the fock operator of equation (4.3).

\[
\frac{\delta \langle \phi_H | \hat{f} | \phi_H \rangle}{\delta c_p} = - \sum_{k \neq H} \left\langle \phi_H | \hat{f} | \phi_k \right\rangle \frac{\langle \phi_k | f_p | \phi_H \rangle}{\epsilon_k - \epsilon_H} \\
- 2 \sum_{j \neq k}^{\text{occ}} \langle \phi_H \phi_H | \phi_j \phi_k \rangle \frac{\langle \phi_k | f_p | \phi_j \rangle}{\epsilon_k - \epsilon_j} \\
+ \sum_{j \neq k}^{\text{occ}} \langle \phi_H \phi_k | \phi_j \phi_H \rangle \frac{\langle \phi_k | f_p | \phi_j \rangle}{\epsilon_k - \epsilon_j} + \text{c.c.} \tag{4.22}
\]

Finally, we note that the second and the third term of the above equation are antisymmetric with respect to j and k. Consequently, the sum over k runs only over virtual orbitals. We change the signs of each term by changing the denominator from \((\epsilon_k - \epsilon_j)\) to \((\epsilon_j - \epsilon_k)\).
4.1. METHOD AND COMPUTATIONAL DETAILS

\[
\frac{\delta \langle \Phi_H | \hat{f} | \Phi_H \rangle}{\delta c_p} = \sum_{k \neq H} \langle \Phi_H | \hat{f} | \Phi_k \rangle \frac{\langle \Phi_k | f_p | \Phi_H \rangle}{\varepsilon_H - \varepsilon_k} \\
+ 2 \sum_{j \text{occ}} \sum_{k> H} (\Phi_H \Phi_H | \Phi_j \Phi_k) \frac{\langle \Phi_k | f_p | \Phi_j \rangle}{\varepsilon_j - \varepsilon_k} \\
- \sum_{j \text{occ}} \sum_{k> H} (\Phi_H \Phi_k | \Phi_j \Phi_H) \frac{\langle \Phi_k | f_p | \Phi_j \rangle}{\varepsilon_j - \varepsilon_k} + c.c. \quad (4.23)
\]

Combining equations (4.23) and (4.8) and assuming real orbitals we obtain

\[
\frac{\partial \Delta}{\partial c_p} = 2 \sum_{j \neq H} \langle \Phi_H | \hat{f} | \Phi_j \rangle \frac{\langle \Phi_H | f_p | \Phi_j \rangle}{\varepsilon_H - \varepsilon_i} \\
+ \sum_{j \text{occ}} [2 (\Phi_H \Phi_H | \Phi_j \Phi_i) - (\Phi_H \Phi_i | \Phi_j \Phi_H)] \\
\times \frac{\langle \Phi_i | f_p | \Phi_H \rangle}{\varepsilon_j - \varepsilon_i} - \langle \Phi_H | f_p | \Phi_H \rangle \quad (4.24)
\]

In a rigorous penalty function procedure the limit \( \lambda \to \infty \) provides the solution. In practice, however, one can use a high enough value for \( \lambda \) to satisfy the HOMO condition, Equation (4.4), with the required precision.

The method described above is implemented in a new program. It is written in Python [78] using routines from the Scipy [79] and PyQuante [80] packages. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimizer of the Scipy package is used to find the energy minimum. The gradient is calculated with Equations (4.2) and (4.7), respectively. The energy is considered to be converged if the length of the gradient vector is less then \( 10^{-8} \) for the two-electron systems and less than \( 10^{-6} \) in the other cases.
CHAPTER 4. PRECISION OF TOTAL ENERGY AND ORBITAL ENERGY

The nine basis sets in use are STO-3G (I, [89]), 6-31G(II, [90]), 6-31G** (III, [90]), cc-pVDZ (IV, [81, 82]), cc-pVTZ without f (V, [81, 82]), uncontracted cc-pVTZ without f (VI, [81, 82]), uncontracted cc-pVQZ without f (VII, [81, 82]), uncontracted cc-pV5Z without f (VIII, [81, 82]) and Partridge 3 (IX, [91]). The Partridge 3 basis set is an even tempered basis set, which includes only s functions. There are no Partridge 3 basis functions for He available so that the basis functions for Be are used.

4.2 Basis set dependence

In this Section the basis set dependence of EXX is investigated for the crudest choice of \( v_0(r) \). The zero Reference potential \( v_0(r) = 0 \) is chosen, so that the basis set expansion in Equation (2.68) has to build-up the whole potential \( v_{ee}(r) \) from scratch and the HOMO condition Equation (4.4) is not imposed. To check the performance of the current implementation of EXX in this situation, the energies EXX are calculated for the prototype few electron systems Be, Ne, LiH, and HF. The EXX values calculated in the uncontracted correlation-consistent triple zeta cc-pVTZ basis of Gaussian type orbitals (with the f-functions excluded) for both the EXX orbitals and the potential are compared in Table 4.1 with the HF energies \( E^{HF} \). The latter provide a lower bound to the former. The positive differences between \( E^{EXX} \) and \( E^{HF} \) in Table 4.1 are rather small and they are close to the corresponding literature data [36, 44], indicating the proper performance of our implementation.

The basis set dependence is analyzed in the two-electron case, in which the exact \( E^{EXX} \) must coincide with \( E^{HF} \). Table 4.2 presents \( E^{HF} \) calculated for the two-electron atom He and the molecule \( \text{H}_2 \) (at the experimental equilibrium bond distance of 1.401 Bohr) in nine different basis sets (see Section 4.1). The \( E^{HF} \) values are nu-
4.2. BASIS SET DEPENDENCE

Table 4.1: Energy differences between EXX and HF in mH

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.59</td>
<td>0.58</td>
<td>0.58</td>
<td>0.82</td>
<td>0.82</td>
</tr>
<tr>
<td>Ne</td>
<td>1.5</td>
<td>1.7</td>
<td>1.7</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>LiH</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>3.00</td>
<td>1.99</td>
<td>2.00</td>
<td>2.28</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Orbital and Potential basis set: uncontracted cc-pVTZ without f

Numerically precise to at least the 10 digits shown in the table. Comparison of the $E^{HF}$ values for different basis sets to the basis set limit values shows, that a “good” basis set like cc-pVTZ achieves a “physical accuracy” (deviation from basis set limit) of better than $10^{-3}$, and only the largest basis sets (cc-pV5Z and Partridge-3) achieve an accuracy better than $10^{-4}$.

Tables 4.3 and 4.4 compare the energy differences ($E^{EXX} - E^{HF}$) obtained for He and H$_2$ in the various basis sets, where $E^{EXX}$ does not refer to the exact $E^{EXX}$ values in the given orbital basis, which would be identical to the HF one. $E^{EXX}$ refers to the approximate values obtained with the limited expansion of the potential. Different columns of the tables correspond to different orbital basis sets, while each row collects the ($E^{EXX} - E^{HF}$) values obtained when the functions of one of these basis sets are used as the expansion functions $\{g_i(r)\}$ for the potential.

The results of Tables show 4.3 and 4.4 that even with the crudest set-up (no Reference potential $v_0(r)$) the adopted EXX scheme is able to produce accurate total energies $E^{EXX}$. For the smaller orbital basis sets II-IV (in the case of He) and I-II (in the case of H$_2$),
**Table 4.2:** HF energies in Hartree for He and H$_2$ with different basis sets for orbital expansion

<table>
<thead>
<tr>
<th>Basis</th>
<th>He</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-1.1167143775</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>-2.8551604036</td>
<td>-1.1267426778</td>
</tr>
<tr>
<td>III</td>
<td>-2.8571330547</td>
<td>-1.1312843370</td>
</tr>
<tr>
<td>IV</td>
<td>-2.8551604547</td>
<td>-1.1287094343</td>
</tr>
<tr>
<td>V</td>
<td>-2.8611535515</td>
<td>-1.1329814808</td>
</tr>
<tr>
<td>VI</td>
<td>-2.8611536289</td>
<td>-1.1330819445</td>
</tr>
<tr>
<td>VII</td>
<td>-2.8615153771</td>
<td>-1.1334689562</td>
</tr>
<tr>
<td>VIII</td>
<td>-2.8616275406</td>
<td>-1.1336094057</td>
</tr>
<tr>
<td>IX</td>
<td>-2.8616614665</td>
<td></td>
</tr>
<tr>
<td>Exact</td>
<td>-2.86168 [92]</td>
<td>-1.133629 [93]</td>
</tr>
</tbody>
</table>

Characterization of the bases is found in Section 4.1.
4.3 Reference potential dependence

In the two-electron case not only the total energy $B_{EXX}$, but the complete EXX solution is exactly known. In this case the electronic potential $v_{ee}(r)$ is equal to the Coulomb potential of a single electron density of an electron in the occupied HF orbital $\phi_i^{HF}$, which in this particular case (N=2) is equivalent to the Fermi-Amaldi potential

$$v^{FA}(r) = \frac{N - 1}{N} \int \frac{\rho_0(r_1)}{|r - r_1|} dr_1$$  \hspace{1cm} (4.25)

calculated with the HF density $\rho^{HF}(r)$

$$v_{ee}(r) = \int \frac{|\phi_i^{HF}(r_1)|^2}{|r - r_1|} dr_1 = v^{FA}(\rho^{HF}; r)$$  \hspace{1cm} (4.26)

It is thus possible to obtain the local EXX potential from a converged Hartree-Fock calculation, and to obtain benchmark “exact” EXX orbital energies in the given orbital basis by diagonalization.
Different Potential basis sets. A zero indicates a difference of less than $10^{-12}$. All energies are in Hartree.

Characterization of the bases is found in Section 4.1.

The columns collect the various orbital and potential expansions. Furthermore, differences for He between HF and approximate EXX in Hartree with different potential basis sets are found in different rows. The rows collect the various orbital basis sets. A zero indicates a difference of less than $10^{-12}$. All energies are in Hartree.

Table 4.3: Energy differences for He between HF and approximate EXX in Hartree with different potential basis sets.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>3 \cdot 10^{-9}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>2 \cdot 10^{-8}</td>
<td>6 \cdot 10^{-10}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>III</td>
<td>2 \cdot 10^{-7}</td>
<td>2 \cdot 10^{-9}</td>
<td>7 \cdot 10^{-10}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>IV</td>
<td>2 \cdot 10^{-6}</td>
<td>4 \cdot 10^{-9}</td>
<td>2 \cdot 10^{-10}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>V</td>
<td>8 \cdot 10^{-9}</td>
<td>1 \cdot 10^{-5}</td>
<td>7 \cdot 10^{-9}</td>
<td>2 \cdot 10^{-5}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>VI</td>
<td>8 \cdot 10^{-9}</td>
<td>1 \cdot 10^{-5}</td>
<td>7 \cdot 10^{-9}</td>
<td>7 \cdot 10^{-5}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>VII</td>
<td>8 \cdot 10^{-9}</td>
<td>1 \cdot 10^{-5}</td>
<td>7 \cdot 10^{-9}</td>
<td>7 \cdot 10^{-5}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>VIII</td>
<td>3 \cdot 10^{-3}</td>
<td>3 \cdot 10^{-3}</td>
<td>3 \cdot 10^{-3}</td>
<td>3 \cdot 10^{-3}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>IX</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>
Table 4.4: Energy differences for $H_2$ between HF and approximate EXX in Hartree with different orbital and potential expansions.

<table>
<thead>
<tr>
<th>$H_2$</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0</td>
<td>0.10^{-4}</td>
<td>2.10^{-3}</td>
<td>1.10^{-3}</td>
<td>1.10^{-3}</td>
<td>2.10^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>0</td>
<td>0.10^{-4}</td>
<td>2.10^{-4}</td>
<td>2.10^{-4}</td>
<td>2.10^{-4}</td>
<td>2.10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.10^{-4}</td>
<td>1.10^{-5}</td>
<td>1.10^{-5}</td>
<td>1.10^{-5}</td>
</tr>
<tr>
<td>IV</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.10^{-5}</td>
<td>1.10^{-5}</td>
<td>1.10^{-5}</td>
</tr>
<tr>
<td>V</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7.10^{-7}</td>
<td>3.10^{-6}</td>
<td>3.10^{-6}</td>
</tr>
<tr>
<td>VI</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.10^{-9}</td>
<td>3.10^{-7}</td>
</tr>
<tr>
<td>VII</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7.10^{-9}</td>
</tr>
<tr>
<td>VIII</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Different Potential basis sets are found in different rows. The columns collect the various orbital basis sets. A zero indicates a difference of less than $10^{-12}$. All energies are in Hartree. Characterization of the bases is found in Section 4.1.
of the matrix of the KS one-electron operator containing this local potential. The benchmark EXX orbital energies thus obtained are used to assess the performance of various features of the expansion method for the potential. Important issues are the effect of the choice of the fixed reference potential $v_0(r)$ and of the imposed HOMO condition on the precision of the orbital energies $\varepsilon_i$ calculated with the adopted OEP scheme. The reference potentials $v_0(r)$ employed are $v_0(r) = 0$ (as in Section 4.2), the potential of the local density approximation (LDA), $v_0(r) = v^{LDA}_{ee} \left( \left[ \rho^{LDA} \right] ; r \right) = v^{LDA}_{Coul} \left( \left[ \rho^{LDA} \right] ; r \right) + v^{LDA}_{xc} \left( \left[ \rho^{LDA} \right] ; r \right)$, as well as two potentials with Coulombic asymptotics. One of these latter potentials is the FA potential of Equation (4.25). In order to simulate the situation in the general N-electron case, in which the reference potential $v^{FA}(r)$ does not immediately yield the exact $v_{ee}(r)$, the density $\rho_0(r)$ in Equation (4.25) has been obtained with the solutions $\phi_0(r)$ of the one-electron equations with the bare external potential $v_{ext}(r)$, so that this $\rho_0(r)$ is rather different from $\rho^{HF}(r)$. Another potential with the correct asymptotics chosen, is the Yukawa type potential

$$v^Y(r) = \frac{(N - 1) + \exp \left[ - |r - R_A| \right]}{|r - R_A|} \quad (4.27)$$

where $|r - R_A|$ is the distance of the reference electron distance to the center of mass.

Tables 4.5 and 4.6 present the EXX $\varepsilon_i$ calculated for He and H$_2$ in the Partridge 3 basis with the various choices for $v_0(r)$. Though the total energies $E^{EXX}$ are accurately reproduced with all $v_0(r)$, for any $v_0(r)$ the converged $\varepsilon_i$ values exhibit a (mostly) large common shift. For example, for the He orbital energies obtained with $v_0(r) = v^{LDA}_{ee}(r)$ this shift amounts to 0.25 H compared to the accurate EXX values. Though being reduced for $\varepsilon_i$ with the potential $v^{FA}(r)$ with correct asymptotics, this shift is still noticeable
4.3. REFERENCE POTENTIAL DEPENDENCE

(about 4 mH). This result is not consistent, being rather basis set dependent. With the basis VI (both for orbitals and potential) for instance, also the choice \( v_0 (r) = v^{PA} (|\rho_0|, r) \) leads to large shifts (ca. -0.22 H) in the orbital energies. The shift in the Yukawa case is then ca. -0.85 H! The origin of the trouble is the fact that the EXX potential is defined up to an arbitrary constant. This constant is usually fixed by choosing the potential to go to zero at infinity. Though the EXX potential \( v_{ee} (r) \) has zero long-range asymptotics due to the zero asymptotics of the potentials \( v_0 (r) \) used and due to the exponential decay of the basis functions \( g_t (r) \), still a large and virtually uncontrolled shift of \( v_{ee} (r) \) can develop in the molecular bulk region during optimization of \( b_t \). This must lead to an ill-shaped potential in the far outer region, since asymptotically the potential is forced to go to zero. However, the resultant deficient form of \( v_{ee} (r) \) in the outer region affects the orbital shapes in that region, but this has extremely little effect on the energy. It can also be compensated with accompanying small distortions of the final \( v_{ee} (r) \) in the bulk region. The net result is that numerically very precise total energies (far below the physical accuracy of the basis set) are obtained, with still orbital energies that exhibit shifts that are several orders of magnitude larger. Apparently, since total energies can be obtained to very high numerical precision, it is numerically not possible to prevent the shifts in the orbital energies.

Imposing the condition Equation (4.4) with Equation (4.5) solves the problem of the shifts. Tables 4.7 and 4.8 present \( \varepsilon_i \) calculated for He and \( \text{H}_2 \) with the imposed HOMO condition. Due to the fixing with the penalty function according to Equation (4.5), the same HOMO energy is obtained for all choices of fixed potential \( v_0 (r) \) to within \( 10^{-6} \) H. Note that even if we impose by choosing a large \( \lambda \) the HOMO condition to a high precision (better than \( 10^{-10} \)), this does not enforce equality of the HOMO orbital energy in all cases to the
CHAPTER 4. PRECISION OF TOTAL ENERGY AND ORBITAL ENERGY

Table 4.5: Energies in Hartree for He

<table>
<thead>
<tr>
<th>$v_0$</th>
<th>Total energy</th>
<th>1s</th>
<th>2s</th>
<th>3s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>-2.86166146</td>
<td>-1.07828</td>
<td>-0.310563</td>
<td>-0.139064</td>
</tr>
<tr>
<td>LDA</td>
<td>-2.86166133</td>
<td>-0.668139</td>
<td>0.044362</td>
<td>0.183746</td>
</tr>
<tr>
<td>Amaldi</td>
<td>-2.86166147</td>
<td>-0.914369</td>
<td>-0.155224</td>
<td>-0.002898</td>
</tr>
<tr>
<td>Yukawa</td>
<td>-2.86166107</td>
<td>-0.933284</td>
<td>-0.153217</td>
<td>-0.012001</td>
</tr>
<tr>
<td>EXX</td>
<td>-2.86166147</td>
<td>-0.917953</td>
<td>-0.157850</td>
<td>-0.004165</td>
</tr>
</tbody>
</table>

Orbital and potential basis: IX. First column specifies the choice of $v_0$ (except for the row EXX containing the exact EXX results in this basis)

Table 4.6: Energies in Hartree for H$_2$

<table>
<thead>
<tr>
<th>$v_0$</th>
<th>Total energy</th>
<th>$1\sigma_g$</th>
<th>$1\sigma_u$</th>
<th>$2\sigma_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>-1.1336094057551</td>
<td>-0.840566</td>
<td>-0.3999461</td>
<td>-0.337277</td>
</tr>
<tr>
<td>LDA</td>
<td>-1.1336094057549</td>
<td>-0.381889</td>
<td>0.052714</td>
<td>0.113549</td>
</tr>
<tr>
<td>Amaldi</td>
<td>-1.1336094057416</td>
<td>-0.590106</td>
<td>-0.152586</td>
<td>-0.091409</td>
</tr>
<tr>
<td>Yukawa</td>
<td>-1.1336094057550</td>
<td>-0.561836</td>
<td>-0.120489</td>
<td>-0.071729</td>
</tr>
<tr>
<td>EXX</td>
<td>-1.1336094057552</td>
<td>-0.594653</td>
<td>-0.157193</td>
<td>-0.095791</td>
</tr>
</tbody>
</table>

Orbital and potential basis: VIII. First column specifies the choice of $v_0$ (except for the row EXX containing the exact EXX results in this basis)
4.3. REFERENCE POTENTIAL DEPENDENCE

The equality is nevertheless obtained, as noted, to the quite high precision of $10^{-6}$. At this level of accuracy, it becomes clear that the fact that orbital distortion in the outer region has only such a small effect on the total energy, also shows up in relative shifts of orbital energies, notably in the virtual levels, which are much larger than the error in the total energy. As a consequence, this leads to dependence of the energies $\varepsilon_a$ of virtual orbitals on the reference potential $v_0(r)$ (see tables 4.7 and 4.8). For instance, the 2s level of He with $v_0(r) = 0$ deviates by $10^{-2}$ H from the exact EXX value, while the total energy is equal to within $10^{-8}$ H.

The energies $\varepsilon_a$ of the FA starting potential, $v^{FA} [\rho_0]$, stand out as being closer to the corresponding benchmark energies of $v^{FA} [\rho^{HF}]$ than those of notably the zero and LDA potentials. The mutual resemblance of the orbital energies with the starting potential $v^{FA} [\rho_0]$ and the exact EXX potential $v^{FA} [\rho^{HF}]$ is, perhaps, not too surprising, because in this case the starting FA potential, even if used with a different density than the converged one, may be particularly well shaped. We cannot test this property of $v_0(r) = v^{FA} [\rho_0]$ on more general molecules, since for precisely the same reason that $v^{FA} [\rho^{HF}]$ is exact for (only) two electron systems, which allows us to obtain the exact EXX orbital energies, $v^{FA} [\rho_0]$ is such a good starting potential for just these systems.

We note in passing that tables 4.7 and 4.8 allow to compare the HF orbital energies $\varepsilon_i^{HF}$ (first row) with the “exact” EXX (in the same basis) $\varepsilon_i$ (last row). While the HOMO energies $\varepsilon_H$ and $\varepsilon_H^{HF}$ coincide, there is a qualitative difference between the virtual parts of the EXX and HF spectra. The energies $\varepsilon_a$ of virtual EXX orbitals $\phi_a$ are much lower in energy. This trend reflects the well known difference between virtual parts of the KS and HF orbital spectra.
CHAPTER 4. PRECISION OF TOTAL ENERGY AND ORBITAL ENERGY

Table 4.7: Energies in Hartree for He with HOMO condition

<table>
<thead>
<tr>
<th>$v_0$</th>
<th>Total energy</th>
<th>1s</th>
<th>2s</th>
<th>3s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-2.86166146654</td>
<td>-0.917953075</td>
<td>0.046562</td>
<td>0.223471</td>
</tr>
<tr>
<td>Zero</td>
<td>-2.86166146353</td>
<td>-0.917960057</td>
<td>-0.166885</td>
<td>-0.031540</td>
</tr>
<tr>
<td>LDA</td>
<td>-2.86166130244</td>
<td>-0.917951129</td>
<td>-0.132021</td>
<td>0.947204</td>
</tr>
<tr>
<td>Amaldi</td>
<td>-2.86166146158</td>
<td>-0.917952421</td>
<td>-0.157702</td>
<td>-0.004145</td>
</tr>
<tr>
<td>Yukawa</td>
<td>-2.86166109928</td>
<td>-0.917954162</td>
<td>-0.142704</td>
<td>-0.005862</td>
</tr>
<tr>
<td>EXX</td>
<td>-2.86166146654</td>
<td>-0.917953075</td>
<td>-0.157850</td>
<td>-0.004165</td>
</tr>
</tbody>
</table>

Orbital and potential basis: IX. First column specifies (except for the rows with HF and exact EXX results) the choice $v_0(r)$.

Table 4.8: Energies in Hartree for H₂ with HOMO condition

<table>
<thead>
<tr>
<th>$v_0$</th>
<th>Total energy</th>
<th>$1\sigma_g$</th>
<th>$1\sigma_u$</th>
<th>$2\sigma_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-1.1336094057550</td>
<td>-0.594653</td>
<td>0.115708</td>
<td>0.141383</td>
</tr>
<tr>
<td>Zero</td>
<td>-1.1336094057552</td>
<td>-0.594653</td>
<td>-0.161900</td>
<td>-0.102045</td>
</tr>
<tr>
<td>LDA</td>
<td>-1.1336094057552</td>
<td>-0.594653</td>
<td>-0.153790</td>
<td>-0.090312</td>
</tr>
<tr>
<td>Amaldi</td>
<td>-1.1336094057544</td>
<td>-0.594653</td>
<td>-0.156993</td>
<td>-0.095758</td>
</tr>
<tr>
<td>Yukawa</td>
<td>-1.1336094057551</td>
<td>-0.594653</td>
<td>-0.152146</td>
<td>-0.102953</td>
</tr>
<tr>
<td>EXX</td>
<td>-1.1336094057552</td>
<td>-0.594653</td>
<td>-0.157193</td>
<td>-0.095791</td>
</tr>
</tbody>
</table>

Orbital and potential basis: VIII. First column specifies (except for the rows with HF and exact EXX results) the choice $v_0(r)$.
4.3. REFERENCE POTENTIAL DEPENDENCE

In the former case, all KS orbitals feel the same potential of a single electron, while the HF virtual orbitals feel both electrons. This means, that the KS virtual spectrum represents states of an excited electron, while that of HF represents an additional electron. Due to this feature of the KS spectrum, the zero order TD DFT, the difference between the energies of occupied and virtual KS orbitals

$$\omega_0 = \epsilon_a - \epsilon_i$$

yields a fair estimate of the electron excitation energies.

The EXX calculations for the Be atom performed in the Partridge-3 basis (see Table 4.9) with the HOMO condition imposed confirm the conclusions drawn for the two-electron systems. The exact EXX solution for the 4-electron Be atom is not known, however, we can compare the total and orbital EXX energies of various starting potentials \(v_0(r)\) with each other and we can use the HF total energy for Be as the lower bound for the EXX energies \(E^{EXX}\). One can see from table 4.9 that the \(E^{EXX}\) values obtained with various potentials \(v_0(r)\) agree with each other within \(10^{-6}\) Hartree (except when taking the Yukawa potential as starting point) and they are only 0.6 mH higher than \(E^{HF}\). While the energy of the 2s orbital is virtually identical for different \(v_0(r)\) due to the imposed HOMO condition, the energies of the core 1s orbital as well as those for virtual orbitals display noticeable variations. The virtual orbital energies obtained with the potentials \(v^{FA}([\rho_0]; r)\) and \(v^Y(r)\) are closer to each other than to the energies obtained with the zero and LDA potentials. However, the core orbital energies obtained with the zero, LDA and \(v^{FA}([\rho_0]; r)\) potentials show only small differences compared to the one obtained with the \(v^Y(r)\) potential. This difference may be related to the observed smaller accuracy of the total energy calculated with \(v^Y(r)\) as the reference potential. We tentatively conclude that the preference for the FA potential Equation (4.25) as the fixed reference potential \(v_0(r)\), which emerged from the two-electron case, may hold in the general N electron case.
Tables 4.7 and 4.8 display clearly a serious numerical problem of EXX, which emerges already in the two-electron case. Indeed, all reference potentials $v_0(r)$ lead to excellent EXX energies for He. In all cases the calculated total energies $E_{\text{EXX}}$ coincide with six decimal digits with the exact EXX energy (see table 4.7). In addition, due to the HOMO condition Equation (4.4) imposed with the penalty function procedure of Equation (4.5), all energies $\epsilon_H$ coincide, at least with five decimal digits, with the exact (HF) value. However, the errors of the calculated energies $\epsilon_a$ of the virtual orbitals are many orders of magnitude larger than the total energy errors. In some cases (depending on $v_0(r)$ and the type of orbital) the $\epsilon_a$ errors substantially exceed the conventional spectroscopic accuracy of 1 mH, which makes the application of EXX in TD DFT questionable. From the present small sample data, it appears that the Fermi-Amaldi potential might lead to errors that remain within the precision of ca. 1 mH, which is required for meaningful application in TD DFT.

We have argued above that the source of the errors in the orbital energies is caused by the very small effect that the shapes of the orbitals in the far outer region of the molecule have on the energy. The implication would be that if we were able to push the numerical precision of the calculations, and the convergence of the total energy, to ever higher number of digits, the behavior of the potentials and the orbitals in the far outer region will at some point start to matter at the precision to which the total energy is obtained. Inevitably, then, the precision of the orbital energies will increase. However, our numerical evidence is not sufficient to demonstrate this point. Indeed, we can not even rule out that there is an inherent instability of the solution Equation (4.2) for the orbital energies. Taking the orbital energies $\epsilon_i$, which appear on the right hand side


Table 4.9: Energies in H for Be with HOMO condition

<table>
<thead>
<tr>
<th>$v_0$</th>
<th>Total energy</th>
<th>1s</th>
<th>2s</th>
<th>3s</th>
<th>4s</th>
<th>5s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-14.5730225676</td>
<td>-4.732669</td>
<td>-0.309269</td>
<td>0.075784</td>
<td>0.361733</td>
<td>1.098082</td>
</tr>
<tr>
<td>Zero</td>
<td>-14.5724459564</td>
<td>-4.127694</td>
<td>-0.309214</td>
<td>-0.104843</td>
<td>0.121181</td>
<td>0.805336</td>
</tr>
<tr>
<td>LDA</td>
<td>-14.5724413043</td>
<td>-4.125325</td>
<td>-0.309216</td>
<td>-0.072668</td>
<td>0.164397</td>
<td>0.806566</td>
</tr>
<tr>
<td>Amaldi</td>
<td>-14.5724409824</td>
<td>-4.124902</td>
<td>-0.309219</td>
<td>-0.078888</td>
<td>0.152212</td>
<td>0.806078</td>
</tr>
<tr>
<td>Yukawa</td>
<td>-14.5721966794</td>
<td>-4.101876</td>
<td>-0.309154</td>
<td>-0.075315</td>
<td>0.153440</td>
<td>0.807254</td>
</tr>
</tbody>
</table>

Orbital and potential basis: IX. First column specifies (except for the row with HF results) the choice of $v_0$. 
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of Equation (4.2), as the parameters which characterize the solution, the exact solution defines the set \( \left[ E^{E_{XX}}_e, \{ \varepsilon^e_i \} \right] \). The EXX solution can be identified as stable with respect to a certain \( \varepsilon_i \), if for any arbitrary \( \varepsilon > 0 \) there exists \( \delta > 0 \) such that for an approximate solution \( \left[ E^{E_{XX}}_0, \{ \varepsilon^0_i \} \right] \), it follows from \( \left| E^{E_{XX}}_0 - E^{E_{XX}}_e \right| < \delta \) that \( |\varepsilon^0_i - \varepsilon^e_i| < \varepsilon \). Our results do not rule out instability of the EXX solution, since even for the extremely small \( \delta \approx 10^{-13} \) our numerical procedure indicates that \( \varepsilon \) for some orbital energies exceeds the required spectroscopic accuracy of 1 mH. Nevertheless, selection of an appropriate \( v_0(r) \) with correct asymptotics appears to reduce the gap between \( \delta \) and \( \varepsilon \).

4.4 Conclusions

In this Chapter, the performance of the expansion method for the local Kohn-Sham potential to solve the OEP problem [35, 36] has been assessed in an application to the EXX model. The total and orbital EXX energies obtained in various basis sets and with various reference potentials have been compared (for He and H\(_2\)) with those of the exact two-electron solution.

With quasi-Newton optimization of the expansion coefficients of the EXX potential, the procedure produces reliable total energies even with the zero reference potential. In order to reproduce \( E^{HF} \) in a given basis with full numerical precision, at least the same quality basis sets are required for the orbitals and the potential in EXX calculations. However, to reproduce the energy in a given basis set with a physically meaningful accuracy, which may be taken as the basis set error of \( E^{HF} \) in the same orbital basis, a smaller basis for the potential is sufficient.

A serious problem of the OEP method is the reliability of the calculated orbital energies. Without the imposed HOMO condition
even the use of reference potentials with the correct asymptotics can not prevent a large uncontrolled shift of the orbital energies. This reflects the fact that the EXX potential is defined up to an arbitrary constant, while its asymptotics has little influence on the total energy, which is the defining characteristic of the EXX solution. Imposing the HOMO condition within the penalty function procedure solves this problem.

However, even with the HOMO condition imposed, the accuracy of other orbital energies is, typically, many orders of magnitude lower than that for the total energies. This trend might signal possible instability of the EXX solution. This means, that a perfect EXX solution (judging from the total energy and $\varepsilon_H$) is produced with EXX potentials of slightly different form, which is reflected in the different energies of their core (in the case of Be) and virtual orbitals. As was pointed out, other OEP methods also suffer from instability of the orbital energies, so that the instability with respect to (some) orbital energies appears to be an inherent property of the OEP method. A practical step towards diminishing this problem is the selection of a reference potential with Coulombic long-range asymptotics, for example the Fermi-Amaldi potential, as was applied by Yang and Wu [36, 37], which reduces the gap between the errors of the total energy and the orbital energies. This approach is at this point only pragmatic, and it remains to be established whether for general N-electron systems this method is foolproof.
Unphysical Results with Balanced Basis Sets

In the previous Chapter (Chapter 4) it is argued to balance the orbital and potential basis set. To obtain a physically meaningful accuracy a potential basis smaller than the orbital basis suffices. With balanced basis sets correct total energies are obtained but the accuracy of orbital energies is still many orders of magnitude lower than that of the total energy. Recently, schemes to obtain both, accurate total energies and accurate orbital energies, have been proposed [30, 31, 42, 45]. Hesselmann et. al. [42] propose a scheme to balance the orbital and potential basis sets. Two exact conditions were imposed on the Exact Exchange Functional (EXX).

In this Chapter the balanced basis sets of Reference [42] are employed with the Corrected Hartree Functional with $\varepsilon_i$ dependence (CH-$\varepsilon$) from Section 2.5.3. Section 5.1 presents the equations needed for the direct minimization method from Section 2.6.2. Two constraints, similar to the ones employed in Reference [42], are introduced. The exponents of the balanced basis sets are presented. Section 5.2 presents the results of calculations performed on Be and Ne for the CH-$\varepsilon$ functional with balanced basis sets.

In contrast to the results found with unbalanced basis sets the total energies do not break down. However, an unphysical orbital
spectrum is observed. For Be degeneracy of HOMO and LUMO is found. In the case of Ne the 3s orbital energy is even lower than the 2p orbital energy. Consequently, the set of 2p orbitals, consisting of 2p_x, 2p_y and 2p_z, comprises HOMO and LUMO. An exact degeneracy of HOMO and LUMO follows. Moreover, an unphysical potential is obtained. It displays oscillations. To obtain a finite HOMO-LUMO gap, a new functional is defined in Section 5.3. The fictitious occupations are included in all parts of the energy functional. It is concluded that virtual orbitals should enter all energy components of an energy functional.

5.1 Method and Computational Details

In this Section the equations for the direct optimization method of section 2.6.2 utilizing the Corrected Hartree Functional with ε_i dependence (CH-ε) from Section 2.5.3 are derived. The xc functional of CH-ε reads

$$E_{xc}^{CH-\varepsilon} = -\sum_{i,j} w_i w_j (\phi_i | \phi_j \rangle)$$

where the weights \( w_i \) are obtained from fictitious occupation numbers of the KS orbitals.

$$w_i = \sqrt{\bar{n}_i}$$

The \( \bar{n}_i \) are determined with the orbital energies \( \varepsilon_i \) from a Fermi-type distribution

$$\bar{n}_i = \frac{2}{1 + \exp \left( \frac{\varepsilon_i - \varepsilon_F}{\tau} \right)}$$

where \( \varepsilon_F \) is obtained from the condition \( \sum_i \bar{n}_i = N \) and \( \tau \) is a two-parameter function of the HOMO-LUMO gap \( (\varepsilon_L - \varepsilon_H) \).
Plots for Equation (5.3) are given. The solid curve is calculated with a finite HOMO-LUMO gap. The dotted curve is calculated with zero HOMO-LUMO gap.

\[ \tau = \sqrt{a (\varepsilon_L - \varepsilon_H) + b (\varepsilon_L - \varepsilon_H)^2} \] (5.4)

Figure 5.1 shows plots of the Fermi-type distribution (5.3) for zero and finite HOMO-LUMO gaps.

For the direct optimization method the electronic potential is decomposed in a reference potential \( v_0 (r) \) and a linear combination of M basis functions, \( \{ f_p (r) \} \)
CHAPTER 5. UNPHYSICAL RESULTS WITH BALANCED BASIS SETS

\[ v_{ee}(r) = v_0(r) + \sum_{p}^{M} c_p f_p(r) \]  \hspace{1cm} (5.5)

As a reference potential the Fermi Amaldi potential is chosen. This has proved to give the most reliable orbital energies (see Chapter 4). The electronic potential reads

\[ v_{ee}(r) = \frac{N-1}{N} \int \frac{\rho_{0}^{HF}(r')}{|r' - r|} dr' + \sum_{p}^{M} c_p \int \frac{g_p(r')}{|r' - r|} dr' \]  \hspace{1cm} (5.6)

In contrast to Chapters 3 and 4 the potential functions are defined as

\[ f_p(r) = \int \frac{g_p(r')}{|r - r'|} dr' \]  \hspace{1cm} (5.7)

Where the functions \( g_p(r) \) are Gaussians. The electrostatic potential is used to ensure proper asymptotic behavior.

The electronic potential \( v_{ee}(r) \) (Equation (5.6)) must arise from an electronic charge density that integrates to N-1. It follows that

\[ N - 1 = \frac{N-1}{N} \int \rho_{0}^{HF}(r) dr + \sum_{p}^{M} c_p \int g_p(r) dr \]  \hspace{1cm} (5.8)

Considering that the ground state HF density integrates to N a condition on the expansion coefficients \( c_p \) is formulated

\[ y^T c = 0 \]  \hspace{1cm} (5.9)

with the elements \( y_p \) of vector \( y \) given by

\[ y_p = \int g_p(r) dr \]  \hspace{1cm} (5.10)
5.1. METHOD AND COMPUTATIONAL DETAILS

To meet this constraint the original basis functions are transformed according to

\[ g'_p(r) = g_p(r) - g_{p+1}(r) \cdot y_p/y_{p+1} \quad \forall 1 \leq i \leq M - 1 \quad (5.11) \]
\[ g'_M(r) = g_M(r) - g_1(r) \cdot y_M/y_1 \]

This ensures \( \int g'_p(r) \, dr = 0 \) for all functions.

In Chapter 4 it has been stressed that a condition on the HOMO energy is necessary to prevent large shifts in orbital energies. In the case of CH-\( \varepsilon \) large shifts in orbital energies are prevented by an exact condition on the HOMO energy. It has been shown that the HOMO energy must equal the negative of the first ionization potential [46].

\[ \varepsilon_{HOMO} = -I_p \quad (5.12) \]

The constraint is enforced via a penalty function like in Chapter 4. The CH-\( \varepsilon \) functional is augmented.

\[ L = E^{CH} + \lambda \Delta^2 \quad (5.13) \]

with

\[ \Delta = \varepsilon_{1}^{CH} + I_p \quad (5.14) \]

In general, the limit \( \lambda \to \infty \) has to be taken to exactly satisfy Equation (5.12). However, this constraint is introduced only to prevent large shifts in orbital energies. A value of 100 is enough to fix the orbital energies.

The CH-\( \varepsilon \) functional includes virtual orbitals. It is expected that the largest contribution from the virtual orbitals comes from the
LUMO. In the case of Be this is the 2p orbital. The basis sets for Be from Reference [42] do not include p functions. Consequently, the LUMO cannot be described. To perform meaningful CH-ε calculations on Be the orbital basis set is augmented with p functions. The exponents are taken from the cc-pVQZ [81] basis set. All orbital exponents are shown in Table 5.1.

One may wonder if the augmented orbital basis is still balanced to the potential basis. This is surely the case, because the new orbital set is larger than the originally balanced basis set. Only a truncation of the orbital set could lead to an unbalanced set.

In the case of Ne the LUMO is represented by the 3s orbital. The orbital basis for Ne from Reference [42] includes s and p functions. Hence, the LUMO can be represented by the orbital set. Higher lying virtual orbitals are not needed because degeneracy of HOMO and LUMO is found. This leads to zero fictitious occupations of all higher lying virtual orbitals (compare Figure 5.1).

The method described above is implemented in a new program. It is written in Python [78] using routines from the Scipy [79] and PyQuante [80] packages. The Nelder-Mead (NM) optimizer of the PyQuante package is used to find the energy minimum. A gradient is not needed for the NM optimizer. All calculations were performed with the charge density constraint (Equation (5.8)) and the constraint on the value of the HOMO orbital energy (Equation (5.12)) imposed. The parameters were chosen as in Reference [18], \( a = 0.008 \) and \( b = 0.045 \) (see Equation 5.4). After the energy minimum is found the gradient is calculated with the finite difference method. The energy is considered to be converged if all elements of the gradient vector are less than \( 10^{-4} \).
### 5.1. METHOD AND COMPUTATIONAL DETAILS

#### Table 5.1: Exponents for Orbital basis of Be.

<table>
<thead>
<tr>
<th>Type</th>
<th>Exponent</th>
<th>Type</th>
<th>Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>5000</td>
<td>S</td>
<td>0.30517578125</td>
</tr>
<tr>
<td>S</td>
<td>2500</td>
<td>S</td>
<td>0.152587890625</td>
</tr>
<tr>
<td>S</td>
<td>1250</td>
<td>S</td>
<td>0.0762939453125</td>
</tr>
<tr>
<td>S</td>
<td>625</td>
<td>S</td>
<td>0.0381469726562</td>
</tr>
<tr>
<td>S</td>
<td>312.5</td>
<td>S</td>
<td>0.0190734863281</td>
</tr>
<tr>
<td>S</td>
<td>156.25</td>
<td>S</td>
<td>0.00953674316406</td>
</tr>
<tr>
<td>S</td>
<td>78.125</td>
<td>S</td>
<td>0.00476837158203</td>
</tr>
<tr>
<td>S</td>
<td>39.0625</td>
<td>P</td>
<td>14.03</td>
</tr>
<tr>
<td>S</td>
<td>19.53125</td>
<td>P</td>
<td>3.168</td>
</tr>
<tr>
<td>S</td>
<td>9.765625</td>
<td>P</td>
<td>0.9024</td>
</tr>
<tr>
<td>S</td>
<td>4.8828125</td>
<td>P</td>
<td>0.3036</td>
</tr>
<tr>
<td>S</td>
<td>2.44140625</td>
<td>P</td>
<td>0.113</td>
</tr>
<tr>
<td>S</td>
<td>1.220703125</td>
<td>P</td>
<td>0.04286</td>
</tr>
<tr>
<td>S</td>
<td>0.6103515625</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Types and exponents for orbital basis for Be.
5.2 Unphysical results for the Corrected Hartree Functional with $\varepsilon_i$ dependence (CH-$\varepsilon$)

5.2.1 Be

The minimum total energy for Be is found to be -14.951 H. The value is significantly lower than the full CI value of -14.667 H [94]. Figure 5.2 shows the full KS potential (dash-dotted curve) and its components. The expanded part of the potential (solid curve) exhibits a maximum at the nucleus and a minimum at around 0.5 Bohr. The small oscillations of the expanded potential (solid curve) are not visible in the total KS potential (dash-dotted curve) because it is dominated by the $-4/r$ term of the nuclear potential. Large oscillations are not observed in Figure 5.2. This is a consequence of the balanced basis sets. Nevertheless, the potential basis tries to build up oscillations, which are not as strong as the ones observed in Chapter 3 because the potential basis is smaller.

Table 5.2 gives the orbital energies of the CH-$\varepsilon$ calculation together with the fictitious occupation numbers. The last column gives the exact KS orbital energies taken from Reference [95]. The HOMO (2s) energy is found to be -0.343 H. The negative ionization potential is -0.343 H. The excellent agreement verifies the successful application of condition (5.12).

While the HOMO (2s) energy is in exact agreement with the exact HOMO energy, all other orbital energies are significantly lower than the exact ones. This indicates that a fixing of the HOMO energy does not prevent shifts in the rest of the orbital spectrum. In particular, the LUMO (2p) energy is too low. It is degenerate with the HOMO energy. The difference is in the order of $10^{-8}$ H.
5.2. UNPHYSICAL RESULTS FOR THE CORRECTED HARTREE FUNCTIONAL WITH $\varepsilon_f$ DEPENDENCE

The solid curve displays the expanded potential ($\sum_p c_p f_p(r)$). The dashed curve displays the reference potential $v_0(r) = (N - 1)/N \int \rho_0^{HF}(r')/|r' - r|dr'$. The dotted curve displays the electronic potential $v_{ee}(r)$, which is the sum of the reference potential (dashed curve) and the expanded potential (solid curve). The dash-dotted curve displays the full KS potential, which is the sum of the electronic potential (dotted curve) and the nuclear potential ($-1/r$).
# CHAPTER 5. UNPHYSICAL RESULTS WITH BALANCED BASIS SETS

### Table 5.2: Orbital energies of Be

<table>
<thead>
<tr>
<th>CH-(\varepsilon)</th>
<th>(\bar{n}_i)</th>
<th>Exact[95]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>-5.893</td>
<td>2.00</td>
</tr>
<tr>
<td>2s</td>
<td>-0.343</td>
<td>0.50</td>
</tr>
<tr>
<td>2p</td>
<td>-0.343</td>
<td>0.50</td>
</tr>
<tr>
<td>3s</td>
<td>-0.238</td>
<td>0.00</td>
</tr>
<tr>
<td>3p</td>
<td>-0.201</td>
<td>0.00</td>
</tr>
</tbody>
</table>

All energies are in H. Fictitious occupation numbers as in Equation (5.3).

As a consequence the fictitious occupations for HOMO and LUMO are equal (see Table 5.2). Further virtual orbitals are not occupied, since the HOMO-LUMO gap, which is used to regulate involvement of virtual orbitals (see Equation (5.3) and Figure 5.1), vanishes. Consequently, changing of parameters \(a\) and \(b\) in Equation (5.4) does not change the solution.

During the optimization procedure inversion of the 2s and 2p orbitals occurred frequently. This configuration, however, was discarded because the total energy increases. With an inversion of 2s and 2p orbitals the 2p orbital enters the one electron and Coulomb energy functional. The energy of the one electron functional is lowered by substituting a 2p orbital for a 2s orbital. However, the Coulomb energy increases if the 2p orbital enters the density rather than the 2s orbital. The net effect is an increase of total energy.

The potential found for Be has consequences for the PT2 functional discussed in section 3.2. With a (near) degeneracy of HOMO and LUMO the total energy of PT2 (see Equation (3.6)) collapses. It is noteworthy that this happens even with a balanced poten-
tial basis set. This shows again, that perturbational theory based functionals are not to be used variationally.

### 5.2.2 Ne

The minimum total energy for Ne is -126.741 H. The value is significantly higher than the full CI value of -128.939 H [94]. Figure 5.3 shows plots for the full KS potential (dash-dotted curve) and its components. The expanded part of the potential (solid curve) shows many oscillations. The magnitude of the oscillations is not as large as depicted in figures 3.1 in Chapter 3. However, they are so large that the full KS potential (dash-dotted curve) is repulsive around 2 Bohr. Two shoulders around 0.5 Bohr and 1 Bohr are found in the full KS potential.

Table 5.3 gives the orbital energies of the CH-ε calculation together with the fictitious occupation numbers. An inversion of the 2p and 3s orbital energies is observed. Consequently, the 3s orbital is fully occupied. The set of 2p orbitals, 2pₓ, 2pᵧ and 2pᵦ, contains together four electrons. This means that the 2p set is at the same time the HOMO and the LUMO orbital. Like in the Be case, the virtual orbital energies are too low. In particular the 3s orbital energy is so low that it becomes occupied.

The exact degeneracy of HOMO and LUMO leads to a sharp step in the Fermi-type distribution of Equation (5.3) (see Figure 5.1). Consequently, higher lying virtual orbitals are not occupied. Changing of parameters a and b in Equation (5.4) does not effect the shape of the Fermi-type distribution because the HOMO-LUMO gap is zero.
The solid curve displays the expanded potential \( \sum_p c_p f_p(r) \). The dashed curve displays the reference potential \( v_0(r) = (N - 1)/N \int \rho_0^H(r')/|r' - r| dr' \). The dotted curve displays the electronic potential \( v_{ee}(r) \), which is the sum of the reference potential (dashed curve) and the expanded potential (solid curve). The dash-dotted curve displays the full KS potential, which is the sum of the electronic potential (dotted curve) and the nuclear potential \((-1/r)\).
5.3. A FUNCTIONAL WITH VIRTUAL ORBITALS ENTERING ALL PARTS

Table 5.3: Orbital energies of Ne

<table>
<thead>
<tr>
<th></th>
<th>CH-ε</th>
<th>( \bar{n}_i )</th>
<th>Exact[95]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>-31.219</td>
<td>2.00</td>
<td>-30.816</td>
</tr>
<tr>
<td>2s</td>
<td>-1.687</td>
<td>2.00</td>
<td>-1.652</td>
</tr>
<tr>
<td>3s</td>
<td>-0.870</td>
<td>2.00</td>
<td>-0.795</td>
</tr>
<tr>
<td>2p</td>
<td>-0.805</td>
<td>1.33</td>
<td>-0.183</td>
</tr>
<tr>
<td>3p</td>
<td>-0.726</td>
<td>0.00</td>
<td>-0.110</td>
</tr>
</tbody>
</table>

All energies are in H. Fictitious occupation numbers as in Equation (5.3)

5.3 A Functional with Virtual Orbitals Entering all Parts

From experiences with inclusion of a 2p orbital in all parts of the energy in the case of Be, a new functional is introduced in an ad-hoc fashion without theoretical foundation. To restore the correct spacing between orbitals the fictitious occupation numbers from the CH functional are used in all parts of the energy functional. The new functional is defined as

\[
E^{all} = \sum_i w_i^2 \left\langle \phi_i \left| -\frac{1}{2} \nabla^2 + v_{ext}(r) \right| \phi_i \right\rangle + \sum_{ij} w_i w_j \left\langle \phi_i \phi_j | \phi_i \phi_j \right\rangle \tag{5.15}
\]

The weights, \( w_i \), are determined as in the case of CH (see Equations (5.2), (5.3) and (5.4)). Calculations have been performed for Be with both constraints (Equations (5.6) and (5.12)) applied. The
### Table 5.4: Orbital energies for Be

<table>
<thead>
<tr>
<th>Orbital</th>
<th>ensEXX</th>
<th>$\bar{n}_i$</th>
<th>Exact [95]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>-4.434</td>
<td>2.00</td>
<td>-4.226</td>
</tr>
<tr>
<td>2s</td>
<td>-0.415</td>
<td>1.36</td>
<td>-0.343</td>
</tr>
<tr>
<td>2p</td>
<td>-0.284</td>
<td>0.18</td>
<td>-0.210</td>
</tr>
<tr>
<td>3s</td>
<td>-0.224</td>
<td>0.48</td>
<td>-0.098</td>
</tr>
<tr>
<td>3p</td>
<td>-0.134</td>
<td>0.01</td>
<td>-0.073</td>
</tr>
</tbody>
</table>

Orbital energies and fictitious occupations for ensEXX calculations on Be. Energies are in Hartree.

The same basis sets as for the CH calculations were used. The minimum energy is -14.647 H, which is in good agreement with the full CI value of -14.667 H [94]. The full KS potential (dash-dotted curve) is well behaved (See Figure 5.4). The expansion functions make only small corrections to the reference potential (dashed curve). Only small wiggles are observed in the expanded part of the potential (solid curve). The most interesting results are the orbital energies. Table 5.4 shows the orbital energies and fictitious occupations as well as the exact orbital energies from Reference [95]. A finite HOMO-LUMO gap is found. However, the virtual orbital energies are still too low.

### 5.4 Conclusions

In this Chapter balanced basis sets from Reference [42] were used to perform calculations on the CH-ε functional. The CH-ε functional includes virtual orbitals. The basis set for Be from Reference [42] consists only of s functions. It cannot describe the lowest unoccu-
The solid curve displays the expanded potential \( \sum_p c_p f_p(r) \). The dashed curve displays the reference potential \( v_0(r) = (N - 1)/N \int \rho_0^{HF}(r')/|r' - r| dr' \). The dotted curve displays the electronic potential \( v_{ee}(r) \), which is the sum of the reference potential (dashed curve) and the expanded potential (solid curve). The dash-dotted curve displays the full KS potential, which is the sum of the electronic potential (dotted curve) and the nuclear potential \(-1/r\).
CHAPTER 5. UNPHYSICAL RESULTS WITH BALANCED BASIS SETS

occupied molecular orbital (LUMO) of the system. Consequently, the orbital set is augmented with p functions. In the case of Ne this problem does not occur. The balanced basis set includes s and p functions. All occupied orbitals and the LUMO are represented by s and p orbitals. Hence, additional basis functions are not needed.

For all systems the Optimized Effective Potential (OEP) is calculated. Results obtained with balanced basis sets improve dramatically over those found in Chapter 3. The total energies are at reasonable values in both cases. Figures 5.2 and 5.3 show the different potentials. While the potential of Be is well behaved the potential of Ne displays oscillations. The oscillations are found even with a balanced potential basis. Nevertheless, the oscillations observed are smaller than the ones found with unbalanced basis sets in Chapter 3, verifying the necessity to balance orbital and potential basis. The expansion functions make only small contributions to the total potential. This behavior is ensured by the charge density constraint (Equation (5.8)). The occupied orbitals are at reasonable values. Large shifts are not observed. This is ensured by imposing the HOMO condition (Equation (5.12)).

The virtual orbital spectrum, however, is disastrous. Too low virtual orbital energies are observed. This leads to a degeneracy of 2s and 2p orbitals for Be (Table 5.2). For Ne the 3s orbital energy is so low that it becomes occupied. This leads to an unusual occupancy of the set of 2p orbitals. Each is occupied by 1.33 electrons (Table 5.3). Low lying virtual orbitals are beneficial for the total energy. Small differences between occupied and unoccupied orbitals lead to large fictitious occupations, and hence, to large exchange correlation energies. This effect is observed for a particular version of the CH-ε functional, where the involvement of virtual orbitals is regulated by the HOMO-LUMO gap. However, it is obvious that any scheme that determines the fictitious occupations for the CH-
5.4. CONCLUSIONS

ε functional from the orbital energies will lead to too low virtual orbitals. This is because the total energy benefits from low virtual orbital energies.

The unphysical solutions clearly indicate a fundamental problem of CH-ε. Involvement of virtual orbitals in only the exchange correlation part seems to be the source. In Section 5.3 a new functional is defined in an ad-hoc fashion. It includes virtual orbitals in all parts of the energy functional. A well-behaved potential is obtained with a surprisingly good total energy. The orbital spectrum is improved compared to the CH-ε spectrum. A finite HOMO-LUMO gap is found. Nevertheless, the virtual orbital energies are too low.

While the problem of artificial degeneracy is solved, the problem of too low virtual orbital energies remains. It is fair to believe, that too low virtual orbital energies are a consequence of the definition of the fictitious occupation numbers (see Equations (2.49) and (2.50)). In particular, dependence of the fictitious occupation numbers on the orbital energies seems to be the problem, since too low orbital energies are obtained even with finite HOMO-LUMO gap.

One remedy of too low virtual orbital energies could be a better parametrization of the fictitious occupation numbers. In Section 5.2 the fictitious occupation numbers depend on a Fermi-type distribution that is regulated by the HOMO-LUMO gap. One can imagine to extend the dependence to all occupied an a few or even all virtual orbitals. Another possibility is to drop the HOMO-LUMO gap dependence and replace it with a single parameter that needs to be fitted.

The results of this Chapter emphasize the conclusion drawn in Chapter 3. Orbital Dependent Functionals should include virtual orbitals in all parts of the energy functional. Section 5.3 presents results for a functional that includes virtual orbitals in all parts of the functional. However, it was introduced in an ad-hoc fashion.
Still a rigorous theoretical framework needs to be established. Another obvious choice to include virtual orbitals in all parts of the energy functional is DMFT, which is discussed in the next Part. The newly defined functional from Section 5.3 could also be embedded in DMFT with parametrized occupation numbers rather than optimized occupation numbers.
Part II

Orbital Dependent Functionals in Density Matrix Functional Theory

Geschrieben steht: “im Anfang war das Wort!”
Hier stock’ ich schon! Wer hilft mir weiter fort?
Ich kann das Wort so hoch unmöglich schätzen,
Ich muß es anders übersetzen,
Wenn ich vom Geiste recht erleuchtet bin.
Geschrieben steht: im Anfang war der Sinn.
Bedenke wohl die erste Zeile,
Daß deine Feder sich nicht übereile!
Ist es der Sinn, der alles wirkt und schafft?
Es sollte stehn: im Anfang war die Kraft!
Doch, auch indem ich dieses niederschreibe,
Schon warnt mich was, daß ich dabey nicht bleibe.
Mir hilft der Geist! auf einmal seh ich Rath
Und schreibe getrost: im Anfang war die That!

(Dr. Faust in Faust: Der Tragödie erster Teil
by J.W. von Goethe (1808))
In this Chapter important equations of Density Matrix Functional Theory (DMFT) are derived. In Section 6.1 a generalization of the Hohenberg Kohn Theorem is presented. It proves the existence of an exact functional of the ground state one-particle reduced density matrix (1-RDM). In Section 6.2 properties of the 1-RDM and the natural orbitals and occupation numbers are presented. In Section 6.3 constraints for minimizing the ground state energy are discussed. Finally in Section 6.4 an expression for the effective non-local potential in DMFT is presented.

6.1 Gilbert’s Theorem

In this Section a one-to-one mapping between the ground state wave function and the ground state one-particle reduced density matrix (1-RDM) is proven. This implies the existence of an energy functional of the 1-RDM.

\[ \psi_0(x_1, \ldots, x_N) \Leftrightarrow \gamma_0(x', x) \Rightarrow E_0 \]

The proof runs parallel to that of Hohenberg and Kohn (see Section 2.1.1). As has been shown in Section 1.5 the 1-RDM is a func-
tional of the ground state wave function. It remains to be shown that the wave function is a functional of the 1-RDM.

Consider two distinct non-local potentials \( v(x', x) \) and \( v'(x', x) \), which give two distinct Hamiltonians \( \tilde{H} \) and \( \tilde{H}' \). The associated ground state wave functions \( \psi \) and \( \psi' \) are assumed to be non-degenerate and different. This is a crucial difference to the case of a local potential. Indeed, two distinct non-local potentials may yield the same ground state wave function. This does not mean much, since we want to prove a one-to-one mapping between the ground state wave function and the ground state 1-RDM.

According to the variational principle:

\[
\langle \psi' | \tilde{H} | \psi' \rangle - \langle \psi | \tilde{H} | \psi \rangle = E' + \langle \psi' | \tilde{V} - \tilde{V}' | \psi' \rangle - E > 0 \quad (6.1)
\]

\[
\langle \psi | \tilde{H}' | \psi \rangle - \langle \psi' | \tilde{H}' | \psi' \rangle = E + \langle \psi | \tilde{V}' - \tilde{V} | \psi \rangle - E' > 0 \quad (6.2)
\]

where \( E \) is the ground state energy of \( \psi \) and \( E' \) is the ground state energy of \( \psi' \). Defining the difference of the potentials as \( \delta v(x', x) := v(x', x) - v'(x', x) \) and adding up the above inequalities, yields:

\[
\langle \psi' | \tilde{V} - \tilde{V}' | \psi' \rangle - \langle \psi | \tilde{V} - \tilde{V}' | \psi \rangle > 0 \quad (6.3)
\]

\[
\int \delta v(x', x) \gamma'(x', x) dx' dx - \int \delta v(x', x) \gamma(x', x) dx' dx > 0 \quad (6.4)
\]

\[
\int \delta v(x', x) [\gamma'(x', x) - \gamma(x', x)] dx' dx > 0 \quad (6.5)
\]

The last equation states that the difference of the 1-RDMs must not be zero. This completes the proof of existence of a ground state energy functional of the 1-RDM.
6.2. NATURAL ORBITALS AND OCCUPATIONS

An energy functional of the ground state 1-RDM can be defined as follows:

\[ E[\gamma] = \int \! dx \left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(x) \right] \gamma(x', x)|_{x'=x} + V_{\text{ee}}[\gamma] \]  

(6.6)

The kinetic energy and the energy from the external potential are explicit functionals of the 1-RDM. The remaining electron-electron functional is not explicitly known. Approximations to it are discussed in later Sections. The advantage of DMFT over DFT becomes apparent in Equation (6.6). In DMFT the exact functional of the kinetic energy is known.

Like in DFT a variational principle is formulated. Assume an external potential yielding the Hamiltonian \( \widetilde{H}_0 \) with its ground state 1-RDM, \( \gamma_0(x', x) \), and its ground state wave function, \( \psi_0 \). Inserting a trial 1-RDM

\[ E[\gamma', v] = \langle \psi'| \widetilde{H}_0 | \psi' \rangle \]  

(6.7)

\[ > \langle \psi_0 | \widetilde{H}_0 | \psi_0 \rangle = E[\gamma_0, v] \]  

(6.8)

proves the variational principle.

6.2 Natural Orbitals (NO) and Occupations

In this Section the set of all ground state 1-RDM is characterized. The conditions are known under the name ensemble N-representability conditions.

Consider the eigenequations
The eigenfunctions $\phi_i(x)$ are called natural orbitals (NO) and the eigenvalues $n_i$ are called NO occupation numbers. It is readily verified that the 1-RDM can be expressed as

$$\gamma(x', x) = \sum_i n_i \phi_i^*(x') \phi_i(x)$$  \hspace{1cm} (6.10)$$

The ensemble N-representability conditions read

$$N = \sum_i n_i$$ \hspace{1cm} (6.11)

$$0 \leq n_i \leq 1$$ \hspace{1cm} (6.12)

The energy functional (Equation (6.6)) can now be rewritten in terms of NOs and NO occupations:

$$E[\gamma] = E[\phi_i, n_i] = \sum_i n_i h_{ii} + V_{ve}[\phi_i, n_i]$$ \hspace{1cm} (6.13)

$$h_{ij} = \langle \phi_i | - \frac{1}{2} \nabla^2 + v_{ext}(x) | \phi_j \rangle$$ \hspace{1cm} (6.14)

### 6.3 Minimization of the Energy Functional

In Section 6.1 a variational principle for the energy functional of the 1-RDM is established. The constraints for ensemble N-representability are formulated in Section 6.2. In this Section a minimization procedure is formulated using the method of Lagrangian multipliers.
6.3. MINIMIZATION OF THE ENERGY FUNCTIONAL

The energy functional (Equation (6.6)) is minimized with three constraints imposed. Firstly, the natural orbitals must be orthonormal since they are eigenfunctions of a hermitian kernel. Secondly, the natural occupation numbers must sum up to N. Finally the natural occupation numbers must be between zero and one. The first two conditions are taken into account by the method of Lagrange multipliers:

$$\Omega[\phi_i, n_i] = E[\phi_i, n_i] - \mu(\sum n_i - N) - \sum_{ij} \lambda(\langle \phi_i | \phi_j \rangle - \delta_{ij}) \quad (6.15)$$

The last constraint is enforced by defining $n_i = \cos^2 \theta_i$.

The new functional (Equation (6.15)) must be stationary under variations in $\phi_i$, $\phi_i^*$ and $\theta_i$. Variations in $\phi_i^*$ yield

$$\left(n_i \tilde{h}_i + \frac{1}{\phi_i(x)} \frac{\delta V_{ee}[\phi_i, n_i]}{\delta \phi_i^*(x)} \right) \phi_i(x) = \sum_j \lambda_{ij} \phi_j(x) \quad (6.16)$$

Variations in $\phi_i$ yield analogous equations. Variations in $\theta_i$ yield

$$\sin(2\theta_i) \left(h_{ii} + \frac{\partial V_{ee}[\phi_i, n_i]}{\partial n_i} \right) - \mu = 0 \quad (6.17)$$

The latter equation is fulfilled if $\theta_i = \pi, \pi/2$, which corresponds to $n_i = 0, 1$, or if

$$h_{ii} + \frac{\partial V_{ee}[\phi_i, n_i]}{\partial n_i} = \mu \quad (6.18)$$

With the gradients available the minimum is easily found.
6.4 The Effective Non-Local Potential

If the Lagrangians in Equation (6.16) were diagonal, i.e. $\lambda_{ij} = 0$ for $i \neq j$, Equation (6.16) would be an eigenvalue problem. However, this is not possible. The energy is not invariant under unitary transformations of the natural orbitals. Pernal [96] could still derive equations for an effective non-local potential of the form

$$v_{ee}(x', x) = \sum_i \sum_{j \neq i} \frac{\phi_i(x') \phi_i(x)}{n_i - n_j} \int \left[ \frac{\delta V_{ee}}{\delta \phi_i(x'')} \phi_j(x'') \right] + \sum_i \phi_i(x') \phi_i(x) \frac{\delta V_{ee}}{\delta n_i}$$

(6.19)

$$- \frac{\delta V_{ee}}{\delta \phi^*_i(x'')} \phi^*_i(x'') \right] + \sum_i \phi_i(x') \phi_i(x) \frac{\delta V_{ee}}{\delta n_i}$$

(6.20)

with

$$(\hat{h} + \tilde{v}_{ee}) \phi_i(x) = \epsilon_i \phi_i(x)$$

(6.21)

Equation (6.21) has a surprising property. All natural orbitals with fractional occupation numbers are degenerate at one energy. This is used for efficient DMFT calculations [96].
Available Functionals

In this Chapter currently available functionals in Density Matrix Functional Theory (DMFT) are presented. In contrast to the previous Chapter, in this Chapter we make use of spatial orbitals instead of spin orbitals. Consequently, the natural occupation numbers are between zero and two.

7.1 An almost Exact Functional

For two-electron systems Löwdin and Shull [48] showed that the exact two-electron closed-shell wave function reduces to just a summation over excited closed-shell configurations, when natural orbitals are used as an expansion

\[
\psi(x_1, x_2) = \sum_i c_i |\phi_i(x_1)\phi_i(x_2)| \tag{7.1}
\]

The coefficients can be deduced to obey \( n_i = 2c_i^2 \). Hence, the expansion coefficients are determined by the natural occupation numbers up to a phase factor \( f_i = \pm \)

\[
c_i = f_i \sqrt{n_i/2} \tag{7.2}
\]

The exact pair-density for a two electron system reads
\[ \Gamma^2(r_1, r_2) = 2 \int \Psi(x_1, x_2) \Psi^*(x_1, x_2) \, ds_1 \, ds_2 \]
\[ = \sum_i n_i |\phi_i(r_1)|^2 |\phi_i(r_2)|^2 + \left[ \sum_{a>1} f_a \sqrt{n_1 n_a} \phi_1(r_1) \times \phi^*_a(r_1) \phi_1(r_2) \phi^*_a(r_2) + \sum_{a>b>1} f_a f_b \sqrt{n_a n_b} \phi_a(r_1) \times \phi^*_b(r_1) \phi_a(r_2) \phi^*_b(r_2) \right] + c.c. \]  
\[ (7.3) \]

In Ref. [97] it has been shown that the factors \( f_a \) tend to be negative if \( f_1 \) is chosen to be positive, we arrive at

\[ \Gamma^2(r_1, r_2) = \sum_i n_i |\phi_i(r_1)|^2 |\phi_i(r_2)|^2 + \left[ - \sum_{a>1} \sqrt{n_1 n_a} \phi_1(r_1) \times \phi^*_a(r_1) \phi_1(r_2) \phi^*_a(r_2) + \sum_{a>b>1} \sqrt{n_a n_b} \phi_a(r_1) \times \phi^*_b(r_1) \phi_a(r_2) \phi^*_b(r_2) \right] + c.c. \]  
\[ (7.4) \]

Assuming real orbitals and taking the expectation value we obtain the LS functional

\[ E^{LS} = \sum_i n_i h_{ii} - \sum_{a>1} \sqrt{n_1 n_a} (1a|1a) + \sum_{a>b>1} \sqrt{n_a n_b} (ab|ab) \]  
\[ (7.5) \]

The elements \( h_{ii} \) are the one-electron terms \( \langle i | -\frac{1}{2} \nabla^2 + v_{ext}(r) | i \rangle \). The LS functional is almost exact for two-electron systems. This means that it gives excellent energies for He and the \( \text{H}_2 \) dissociation curve.

### 7.2 JK-only Functionals

In the previous Chapter the existence of an energy functional of the ground state one-particle reduced density matrix (1-RDM) was
7.2. JK-ONLY FUNCTIONALS

established. The electron pair density introduced in Section 1.5 is expressed as

\[
\Gamma^2(r_1, r_2) = \rho_0(r_1)\rho_0(r_2) - \frac{1}{2} |\gamma_0(r_1, r_2)|^2 + C([\gamma]; r_1, r_2) \quad (7.6)
\]

The correlation term \(C([\gamma]; r_1, r_2)\) (see Section 1.6) is in fact the two-particle cumulant in the well-known cumulant expansion of the two-density. Although we will not make any essential use of the cumulant expansion as such, we will conveniently denote it as the two-electron cumulant henceforth. The two-electron cumulant can be written as

\[
C([\gamma]; r_1, r_2) = \sum_{ijkl} c_{ijkl} \phi_i^*(r_1) \phi_j^*(r_2) \phi_k(r_1) \phi_l(r_2) \quad (7.7)
\]

The first successful approximations to \(C([\gamma]; r_1, r_2)\) have been the so-called JK-only functionals. This means that the matrix elements \(c_{ijkl}\) are approximated by the “exchange-like” terms

\[
c_{ijkl} \approx c_{ij} (n_i, n_j) \delta_{jk} \delta_{il} \quad (7.8)
\]

leading to exchange integrals in the energy expression. Specifically, the Coulomb integrals are required for the Hartree functional emerging from the first term of (7.6), while with the approximation (7.8) only exchange integrals are used for the exchange and correlation (xc) functional emerging from the last two terms. Ref. [98] discusses in detail why the correlation effects (both dynamical and nondynamical) can be described with good accuracy with just exchange integrals, and has demonstrated that the Fermi and Coulomb holes can be modeled accurately with an expression of type (7.8).
7.3 The Corrected Hartree (CH) Functional

The first simple functional was derived by Müller [49] from the requirement of minimal violation of the Pauli principle, and by Buijse and Baerends [50, 98] from an analysis of Fermi and Coulomb correlation holes. Csanyi and Arias [51] gave it the name Corrected Hartree (CH), which we will use henceforth. The approximate pair density is calculated with the coefficients

\[ c_{ij}^{CH} = -\sqrt{n_i n_j} + \frac{1}{2} n_i n_j \quad (7.9) \]

The term \( \frac{1}{2} n_i n_j \) annihilates the exchange term in (7.6), so that the term \( -\sqrt{n_i n_j} \) has to take care of all exchange and correlation effects.

This functional describes properly the prototype correlation (static as well as dynamical) in systems such as the (dissociating) \( \text{H}_2 \) molecule and the He-isoelectronic series, when the NOs and NO occupations are used non-selfconsistently [13, 50, 98]. It is less accurate if NOs and occupations are selfconsistently optimized [54, 99]. This is presumably caused by the fact that the CH functional deviated too much from the LS functional (7.4).

7.4 The Goedecker-Umrigar (GU) Correction

The Goedecker-Umrigar (GU) correction [52] omits certain diagonal terms in the summation of Equation (7.9). The coefficients are defined as

\[ c_{ij}^{GU} = \begin{cases} c_{ij}^{CH}, & i \neq j \\ \frac{1}{2} n_i n_j, & i = j \end{cases} \quad (7.10) \]
The GU correction improves total energies compared to CH both for atoms and molecules. In particular, the dissociation region of molecules is improved compared to CH. However, the errors are considerably larger than in the equilibrium region [13, 54, 55].

7.5 Physically Motivated Corrections

Three physically motivated corrections to the CH functional were proposed. They are applied on top of each other, starting with the first and ending with the third [13]. The most successful correction, called C3, requires a preselection of bonding and anti-bonding orbitals.

7.5.1 The first correction (C1)

The first correction restores the positive sign for cross products between different weakly occupied NOs as is the case for the LS functional in Equation (7.4).

\[
c_{ij}^{C1} = \begin{cases} \sqrt{n_i n_j} + \frac{1}{2} n_i n_j, & i > N/2, j > N/2, i \neq j \\ c_{ij}^{C_H}, & \text{otherwise} \end{cases}
\]

This correction preserves the negative sign for the interaction of strongly and weakly occupied orbitals. On top it reconstitutes the proper sign for the interaction of different strongly occupied orbitals as is found in the LS functional (Equation (7.4)).

7.5.2 The second correction (C2)

The second correction changes the interaction between different strongly occupied NOs to an exchange-type interaction.
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(7.12)

\[ c_{ij}^{C2} = \begin{cases} 
0 & , \quad i \leq N/2, j \leq N/2, i \neq j \\
\frac{c_{ij}^{C1}}{i} & , \quad otherwise 
\end{cases} \]

Without C2 correction the interaction between two different strongly occupied orbitals is \(-\sqrt{n_i n_j}\). In the limiting cases of fully occupied orbitals \((n_i = n_j = 2)\) this reduces to the exchange type interaction \(-\frac{1}{2}n_in_j\). With decreasing occupation numbers the exchange type interaction is less negative. It has been inferred [13] that the square root dependence is indeed too negative, because the Coulomb correlation is primarily expressed by the cross terms between strongly and weakly occupied orbitals.

7.5.3 The third correction (C3)

The third correction changes the interaction of the anti-bonding orbital (a) with all strongly occupied except the bonding orbital (b) to an exchange-type interaction. This requires a preselection of the bonding and anti-bonding orbital pair. Furthermore, the interaction for the elements \(c_{ij}\) is changed to an exchange-type interaction for all but the bonding and anti-bonding orbitals.

\[ c_{ij}^{C3} = \begin{cases} 
0 & , \quad b \neq i \leq N/2, j = b \\
0 & , \quad b \neq i = j \neq a \\
\frac{c_{ij}^{C2}}{i} & , \quad otherwise 
\end{cases} \]  

(7.13)

It is a disadvantage of this selective application of the corrections that, in order to use (7.13), one has to select the bonding and anti-bonding NOs prior to calculation. Furthermore, the C3 correction might break the smoothness of the potential energy curve when the
bonding character of NOs changes during dissociation. Moreover, the singling out of the bonding-antibonding pair of orbitals should be generalized to special treatment of the case of strong correlation. Strong correlation manifests itself in occupation numbers differing strongly from 2.0 and 0.0 (even tending to 1.0 from above and below).

### 7.6 The Piris Natural Orbital (PNOF0) Functional

Piris and Leiva [56, 57] proposed the Piris natural orbital functional (PNOF0) based on a detailed consideration of properties of the cumulant. The cumulant for PNOF0 can be represented in the form

\[
\mathcal{C}^{PNOF0}_{ij} = (1 - \delta_{ij}) \mathcal{C}^{C1}_{ij} \tag{7.14}
\]

It uses the C1 correction to the CH functional, except that all diagonal terms are omitted from the cumulant. The results in a cancellation of the diagonal terms of the Coulomb interaction in (7.6), which is equivalent to the GU correction.

An extended form of the PNOF0 functional, denoted PNOF, was proposed by Piris [56]. It was designed to prevent pinning of high occupation number \(n_i \approx 2.0\) at 2.0. However, benchmark calculations [58] have shown, that the simple PNOF0 form performs better than the PNOF.
7.7 The Marques and Lathiotakis (ML) Functional

In Reference [59] a fully empirically functional was derived by Marques and Lathiotakis (ML). The coefficients \( c_{ij}^{ML} \) as a general Padé approximant

\[
c_{ij}^{ML} = \frac{1}{2} x - \frac{1}{2} x \frac{a_0 + a_1 x}{1 + b_1 x}
\]  

(7.15)

where \( x = n_i n_j \). The fraction is multiplied with \( x \) to ensure that the contribution of completely empty states (\( n_i = 0 \)) to the exchange correlation energy is zero. The parameters \( a_0 \), \( a_1 \) and \( b_1 \) were fitted to reproduce the correlation energy of the G2 set [100, 101]. To recover the Hartree-Fock limit in case of integer occupation numbers the parameters are forced to obey

\[
a_0 = 1 + b_1 - a_1
\]

(7.16)

The optimal parameters are

\[
a_0 = 126.3101
\]

(7.17)

\[
a_1 = 2213.33
\]

(7.18)

\[
b_1 = 2338.64
\]

(7.19)
8

The Automatic Version of C3 (AC3)

8.1 Introduction

In Density Matrix Functional Theory (DMFT) [47, 48, 49, 50, 51, 52, 98, 102, 103, 104, 105, 106, 107, 108, 109] the total electronic energy is considered to be a functional $E[\gamma]$ of the ground state one-particle reduced density matrix (1-RDM) $\gamma (r_1, r'_1)$ (throughout this Chapter we consider closed-shell systems)

$$E[\gamma] = E_{oe}[\gamma] + E_{ee}[\gamma]$$

$$\gamma (r_1, r'_1) = \sum_i n_i \phi_i^*(r'_1) \phi_i (r_1)$$

In (8.2) $\chi_i$ are the natural orbitals (NOS) with the occupations $n_i$ and $E[\gamma]$ is the sum of the one-electron $E_{oe}[\gamma]$

$$E_{oe}[\gamma] = -\frac{1}{2} \int \nabla_{r_1}^2 \gamma (r_1, r'_1) |_{r'_1 = r_1} \, dr + \int v_{ext} (r_1) \rho (r_1) \, dr_1$$

and electron-electron interaction $E_{ee}[\gamma]$

$$E_{ee}[\gamma] = \frac{1}{2} \int \frac{\Gamma ([\gamma]; r_1, r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2$$
energies (we use atomic units). In (8.3) \( \rho (r_1) \) is the electron density (diagonal of the 1-RDM) and \( \nu_{\text{ext}} (r_1) \) is the external potential. The exact pair-density functional \( \Gamma[\gamma] \) is not known. We use the usual partitioning in Coulomb, exchange and a rest term (“correlation”),

\[
\Gamma(\gamma; r_1, r_2) = \rho(r_1)\rho(r_2) - \frac{1}{2} |\gamma(r_1, r_2)|^2 + C \left( [\gamma] ; r_1, r_2 \right)
\] (8.5)

When in the exchange term the exact 1-RDM \( \gamma \) is used, as we will do, instead of the Hartree-Fock density matrix \( \gamma^{HF} \), the correlation part of the two-electron energy, \( \frac{1}{2} \int C(r_1, r_2) \, dr_1 \, dr_2 \), is differently defined than in the usual definition of correlation as the energy with respect to the Hartree-Fock energy. The partitioning of the energy according to (8.5) has often been used [50, 110, 111, 112], although it has the disadvantage that the sum rule for the exchange hole that it integrates to -1 now no longer holds. (This can be remedied by working with the best idempotent approximation to \( \gamma \) [113]). It is natural to use (8.5) when the Hartree-Fock model is not taken as a starting point, but the one-matrix is targeted directly. The correlation term \( C \left( [\gamma] ; r_1, r_2 \right) \) is in fact the two-particle cumulant in the well-known cumulant expansion of the two-density, and although we will not make any essential use of the cumulant expansion as such (i.e. to higher orders), we will conveniently denote it as the two-electron cumulant henceforth. The two-electron cumulant can be written as

\[
C \left( [\gamma] ; r_1, r_2 \right) = \sum_{ijkl} c_{ijkl} \phi_i^*(r_1) \phi_j^*(r_2) \phi_k(r_1) \phi_l(r_2)
\] (8.6)

The first successful approximations to \( C \left( [\gamma] ; r_1, r_2 \right) \) have been the so-called primitive functionals [13, 49, 50, 52, 57, 59, 98] presented in
8.1. INTRODUCTION

the previous Chapter. In primitive functionals the matrix elements $c_{ijkl}$ are approximated by the “exchange-like” terms

$$c_{ijkl} \approx c_{ij} (n_i, n_j) \delta_{jk} \delta_{il}$$  \hspace{1cm} (8.7)

leading to exchange integrals in the energy expression. Specifically, the Coulomb integrals are required for the Hartree functional emerging from the first term of (8.5), while with the approximation (8.7) only exchange integrals are used for the exchange and correlation (xc) functional emerging from the last two terms. Ref. [98] discusses in detail why the correlation effects (both dynamical and nondynamical) can be described with good accuracy with just exchange integrals, and has demonstrated that the Fermi and Coulomb holes can be modeled accurately with an expression of type (7.8).

For two-electron systems $\Gamma | \gamma$ is known from the work Löwdin and Shull [48], i.e. the two-density can be written in terms of NOs and NO occupation numbers. Refs. [13, 50, 98] give an approximation to extend the functional to many-electron systems:

$$c_{ij}^{(2)} (n_i, n_j) = f_{ij} \sqrt{n_i n_j} + \frac{1}{2} n_i n_j; \quad f_{ij} = \begin{cases} +1, & i, j (\neq i) > N/2 \\ -1, & \text{otherwise} \end{cases}$$  \hspace{1cm} (8.8)

Molecular dissociation, which is an essentially nonlocal phenomenon, presents a challenging problem for the standard local and semi-local functionals of density functional theory (DFT) [18, 83]. The representation of $C$ in terms of the delocalized canonical NOs $\chi_i$ offers in principle an adequate description of such non-local phenomena. The first NO functional was derived by Müller [49] from
the requirement of minimal violation of the Pauli principle, and by Buijse and Baerends [50, 98] from an analysis of Fermi and Coulomb correlation holes, both in the case of dynamical and nondynamical correlation (see Section 7.3).

\[ c_{ij}^{CH} (n_i, n_j) = -\sqrt{n_i n_j} + \frac{1}{2} n_i n_j \]  \hspace{1cm} (8.9)

The term \( \frac{1}{2} n_i n_j \) annihilates the exchange term in (8.5), so that the \(-\sqrt{n_i n_j}\) term has to take care of all exchange and correlation effects. Gritsenko et. al. [13] introduced a series of three repulsive correction C1, C2 and C3 (see next Section) to the CH functional. The correction C3 introduces explicitly a special treatment of strong (nondynamical) correlation. This requires a preselection of bonding and anti-bonding orbitals.

In this Chapter a DMFT functional is proposed with a fully automatic, occupation number driven, determination of the (approximate) matrix elements of the two-density cumulant. In Section 8.2 the earlier introduced repulsive corrections, culminating in C3, are characterized and the automatic incorporation of these corrections (AC3), leading to an expression for the \( c_{ij} \) of the form

\[ c_{ij}^{AC3} (n_i, n_j) = [1 - D_{ij} (n_i, n_j)] c_{ij}^{CH} \] \hspace{1cm} (8.10)

is presented. In (8.10) \( D_{ij} \geq 0 \) is a parameterized damping function, which assures that \( c_{ij}^{AC3} \) is reduced compared to \( c_{ij}^{CH} \) of (8.9), when appropriate. Unlike C3, the proposed AC3 does not require the manual selection of the bonding and antibonding NOs of a bond. Instead, the \( c_{ij}^{AC3} \) are automatically determined during self-consistent DMFT calculations. In Section 8.3 the results of comparative PNOF0, ML, and AC3 calculations of the potential curves for the dissociating electron pair bond X-H are presented.
8.2. THE AUTOMATIC VERSION OF C3

for the series of the ten-electron hydrides CH$_4$, NH$_3$, H$_2$O, HF as well as for the molecules H$_2$ and HCN. AC3 reproduces well the reference potential curves of the multi-reference configuration interaction (MRCI) method for all interatomic distances X-H in the ten-electron series and HCN. In H$_2$ it has a spurious maximum in the curve at ca. 4 Bohr, but it delivers the correct dissociation limit. PNOF0 and ML perform well close to equilibrium distance, but the E vs R curves go considerably too high at large R, i.e. these functionals seriously underestimate the stability of the molecules when the strong nondynamical correlation occurs that is characteristic of the dissociation (weak bonding) region. In Section 8.4 the conclusions are drawn.

8.2 The Automatic Version of C3 (AC3)

Ref. [13] as a first step introduced the C1 correction to the CH functional (8.9) which restores the positive phase of the cross products between different weakly occupied NOs $(i, j(i \neq i) > N/2)$ in (8.5) as it appears in the two-electron cumulant (see Section (7.1)). With this, C1 employs just that two-electron cumulant, which is exact for the prototypical two-electron systems for dynamical correlation (high Z two-electron ions) and for nondynamical correlation (dissociating two-electron bond)

$$c^{(1)}_{ij}(n_i, n_j) = c^{(2)}_{ij}(n_i, n_j)$$ (8.11)

This implies that $D^{C1} = 0$. The other repulsive corrections are applied on top of C1, and therefore can take the form (8.10) of a damping of the two-electron coefficients $c^{(2)}_{ij}$.

The second correction, C2, eliminates the $c^{(2)}_{ij}$ between different
strongly occupied NOs \((i, j(\neq i) \leq N/2)\), which amounts to reverting to just normal exchange terms, no corrections employing \(\sqrt{n_in_j}\), i.e. \(c_{ij} = 0\) for those NO pairs

\[
c_{ij}^{C2} = \begin{cases} 
0 & , i, j(\neq i) \leq N/2 \\
c_{ij}^{C1} & , otherwise
\end{cases}
\] (8.12)

or

\[
D_{ij}^{C2} = \begin{cases} 
1 & , i, j(\neq i) \leq N/2 \\
0 & , otherwise
\end{cases}
\] (8.13)

[Henceforth, we will simply denote the strongly occupied NOs \((i \leq N/2)\) as “occupied orbitals” and the weakly occupied NOs \((i > N/2)\) as “virtual” or “unoccupied orbitals”.]

In the third step (C3), considered in the case of a \(\sigma\)-bonded molecule, the C2-type correction for off-diagonal occupied \(i, j\) terms is applied also to the products of the virtual antibonding NO \(\chi_a\) of the \(\sigma\)-bond with all strongly occupied NOs, except the bonding NO \(\chi_b\). This requires selection of the antibonding orbital \(\chi_a\) from among the virtuals, and exclusion of the bonding orbital \(\chi_b\) from the set of the occupied NOs \(\{\chi_i\}\) so that all \(c_{ai}^{(2)}\) and \(c_{ia}^{(2)}\) \((i(\neq b) \neq N/2)\) can be eliminated \((D_{ai} = D_{ia} = 0)\). Furthermore, the C2 correction of using full exchange type terms for off-diagonal occupied orbitals (elimination of \(c_{ij}\), \(i, j(\neq i) \leq N/2\)) is now extended to all diagonal (virtual and occupied) coefficients \(c_{ii}\), except those with \(i = a, b\). This implies that the \(i = j\) terms in the exchange energy will have the same prefactor \(\frac{1}{2}n_in_i\) as the diagonal terms in the Coulomb energy, but with minus sign, and therefore will cancel those. [This is not a self-interaction elimination, that is only the case when all \(n_i\) are 0 or 2 as in Hartree-Fock.] This “diagonal” correction has
been applied by Goedecker and Umrigar (GU) [52], but it has been demonstrated that its application to the bonding and antibonding pair of orbitals leads to large errors at long distance [13]. The $c_{ij}^{C3}$ assume the form

$$c_{ij}^{C3} = \begin{cases} 
0 & , i, j \neq i \leq N/2 \\
0 & , i = a, j \neq N/2; j = a, i \leq N/2 \\
0 & , i = j \neq a, \neq b \\
c^{(2)}_{ij} & , otherwise 
\end{cases} \quad (8.14)$$

or

$$D_{ij}^{C3} = \begin{cases} 
1 & , i, j \neq i \leq N/2 \\
1 & , i = a, j \neq N/2; j = a, i \leq N/2 \\
1 & , i = j \neq a, \neq b \\
0 & , otherwise 
\end{cases} \quad (8.15)$$

It is a disadvantage of this selective application of the “off-diagonal” and GU corrections that, in order to use (8.14), one has to select the bonding and antibonding NOs prior to calculation. Furthermore, the C3 correction might break the smoothness of the potential energy curve when the bonding character of NOs changes during dissociation. Moreover, the singling out of the bonding-antibonding pair of orbitals, should be generalized to special treatment of the case of strong correlation, manifesting itself in occupation numbers differing strongly from 2.0 and 0.0 (even tending to 1.0 from above or below).

In order to apply all these strong-correlation types of corrections in an automatic fashion within AC3, we propose to determine the
coefficients $c_{ij}$ by starting with the basic cumulant $c_{ij}^{(2)}$ of the two-electron model, according to C1, and apply the further corrections in a continuous fashion with the damping

$$\left[1 - D_{ij}(n_i, n_j)\right] c_{ij}^{(2)}(n_i, n_j)$$

(8.16)

of $c_{ij}^{(2)}$. To accomplish this, we use the damping function $D_{ij}$ with the following parameterized damping factors $D_d(x)$ and $D_o(x)$ for diagonal terms ($x = n_i - 1$) and off-diagonal terms ($x = n_i + n_j - 2$) respectively

$$D_{ij}(n_i, n_j) = (1 - \delta_{ij}) \Theta(N/2 - i) \Theta(N/2 - j) + \delta_{ij} D_d(n_i - 1) + \Theta(N/2 - j) [1 - \Theta(N/2 - j)] D_o(n_i + n_j - 2)$$

(8.17)

where $D_d$ and $D_o$ are the following rational functions (Padé approximants)

$$D_{d/o}(x) = \frac{P_{d/o}(x)}{1 + P_{d/o}^2(x)}$$

(8.18)

$$P_{d/o} = a_{d/o} x^2 (x^2 - 2)$$

(8.19)

and $\Theta(x)$ is the Heaviside step function [here we define $\Theta(0) = 1$]. These functions are zero around $x = 0.0$ and they approach a constant for $x = \pm 1$, see Figure 8.1 for these functions after the parameter optimization discussed below. The first term in $D_{ij}$ is the C2 correction, i.e. elimination ($D_{ij} = 1$) of the off-diagonal ($1 - \delta_{ij}$) occupied-occupied ($\Theta(N/2 - i) \Theta(N/2 - j)$) cumulant $c_{ij}^{(2)}$, see (8.12). The second term, with damping function $\delta_{ij} D_d(n_i - 1)$, takes care of the C3 correction for the diagonal terms (third entry in Equation

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(8.15)), where \((1 - D_d)\) should effect damping of the \(c_{ii}^{(2)}\) except for the bonding and antibonding orbitals, or in general when the occupation numbers approach 1.0. This can be achieved with a function \(D_d\) obeying \(D_d \approx 1\) when \(n_i \approx 0\) or \(n_i \approx 2\), i.e. \(x = n_i - 1 \approx \pm 1\), and \(D_d \approx 0\) when \(n_i - 1 \approx 0\). The third term in (8.17) applies the remaining C3 correction (second entry of Equation (8.15)), i.e. damping in the cumulant of the \(c_{ii}^{(2)}\) and \(c_{ai}^{(2)}\) off-diagonal coefficients with the factor \((1 - D_o)\) for the cross terms between the antibonding orbital \(a\) with occupied orbitals \(i \leq N/2\), except when \(i\) is the bonding orbital, \(i = b\). In expression (8.17) the \(\Theta\) functions switch this \(D_o\) term on for \((ij)\) an occupied-virtual pair or a virtual-occupied pair. We need two further restrictions: a) among the virtual orbitals only the antibonding orbital (the virtual orbital with significant population \(n_i \uparrow 1.0\)) should be selected; b) amongst the occupied orbitals the bonding partner of \(a\) (the occupied orbital with occupation significantly different from 2.0, \(n_i \downarrow 1.0\)) should be excluded. These restrictions are simultaneously effected with the function \(D_o(n_i + n_j - 2)\): a) Antibonding-occupied pairs: when \(n_i \approx 1\) and \(n_j \approx 2\), or \(n_j \approx 1\) and \(n_i \approx 2\), \(D_o(x \approx 1.0) \approx 1.0\), full damping; b) Other virtual-occupied pairs: when \(n_i \approx 0.0\) and \(n_j \approx 2.0\), or \(n_j \approx 0.0\) and \(n_i \approx 2.0\), \(D_o(x \approx 0.0) \approx 0.0\), no damping, full \(c_{ij}^{(2)}\); c) Antibonding-bonding pair: if both \(n_i\) and \(n_j\) are close to 1.0, \(x = n_i + n_j - 2 \approx 0\) and \(D_o = 0.0\): no damping, full \(c_{ij}^{(2)}\). The optimal parameters \(a_d = 1.4423\) and \(a_o = 1.5552\) in \(D_d\) and \(D_o\) are chosen to reproduce the MRCI energies of the molecules HF and H\(_2\)O at the equilibrium geometry and also when one bond is stretched at \(R(F-H) = 4.0\) and \(R(O-H) = 5.0\) Bohr. These are very few fitting points, but they already yield satisfactory results. The parameters are generated, initially, with a non-linear numerical optimization by the downhill simplex method and their refinement was carried out with the gradient quasi-Newton method of Broyden-Fletcher-
The AC3 damping functions $D_d(n_i - 1)$ and $D_o(n_i + n_j - 2)$.

Goldfarb-Shanno (BFGS). Figure 8.1 displays the functions $D_{d/o}$ calculated with these parameters. Due to the similar values of $a_d$ and $a_o$, the functions $D_d(x)$ and $D_o(x)$ are rather close to each other, displaying only a clear difference near the end points ±1 (see figure 8.1). We have tested the use of a single, averaged, parameter. As a rule, AC3 with different $a_d$ and $a_o$ yields somewhat better results compared to those with a single averaged parameter $a = a_{d/o}$, so that in the next section results with two parameters will be presented.

An important feature of the present AC3 is that, just as the initial CH functional and its C1-C3 corrections, AC3 incorporates the asymptotically correct Heitler-London description of a dissociating
8.2. THE AUTOMATIC VERSION OF C3

single bond (the dissociating \( \text{H}_2 \) molecule) when the occupations \( n_b \) and \( n_a \) of the bonding and antibonding NOs tend towards each other, \( n_b \approx n_a \approx 1 \) [50]. Indeed, by construction, the functions \( D_d \) and \( D_o \) reach their minima at \( n_i = 1 \) and \( n_i + n_j = 2 \), respectively, with both minima being zero, \( D_{d/o}(0) = 0 \), (See Figure 8.1). This means, that the AC3 cumulant (8.10) correctly turns to the paradigmatic \( c_{ij}^{(2)} \) of the exact two-electron cumulant (8.8) in this case. Furthermore, with \( D_o(0) = 0 \) the cumulant \( c_{ij}^{(2)} \) is also retained in the important case of dynamical correlation, which is represented with interaction between the strongly occupied NOs \( \chi_i \) with \( n_i \approx 2 \) and weakly occupied NOs \( \chi_j \) with \( n_j \approx 0 \). We note that the value of the optimized function \( D_d \) in the end points \( x = \pm 1 \) is not 1.0 but 0.64 (see Figure 8.1), so the diagonal part of the C3 correction (third entry of Equation (8.15)) is not fully in effect. The \( c_{ii}^{(2)} \) coefficient in the cumulant for both weakly occupied NOs \( \chi_i \) with \( n_i \approx 0 \) and for strongly occupied core and deep valence NOs \( \chi_i \) with are not completely eliminated but are reduced to ca. 36%. In turn, the off-diagonal part of the AC3 correction, governed by the function \( D_o \) with \( D_o(\pm 1) = 0.71 \) (see Figure 8.1), reduces in the cumulant the \( c_{ai}^{(2)} \) coefficients between the antibonding NO \( \chi_a \) with \( n_i \approx 1 \) and strongly occupied NOs \( \chi_i \) with \( n_i \approx 2 \) by a factor of 0.29 instead of eliminating them as in the original C3 correction.

Figure 8.2 compares the AC3 and C3 potential energy curves for the HF molecule with the reference MRCI one (See the next section for the computational details). AC3 yields consistently higher energies than C3 and on average it improves the agreement between DMFT and MRCI, which is especially true in the dissociation region of 4-5 Bohr (see figure 8.2). A possible reason for this latter improvement is that a relatively high value \( D_o(-1) = 0.71 \) reduces the cumulant \( c_{bj}^{(2)} \) coefficients between the bonding NO \( \chi_b \) with \( n_b \approx 1 \)
Figure 8.2: Dissociation curve of HF

Energy curves for the molecule HF calculated with the DMFT functionals C3, AC3 and the MRCI method.
8.3. COMPARATIVE AC3 CALCULATIONS OF THE POTENTIAL ENERGY CURVES

and weakly occupied NOs \( \chi_j \) with \( n_j \approx 0 \) in AC3, while in the original C3 the full \( c_{ij}^{(2)} \) is retained in this case.

The AC3 modulation of the \( c_{ij}^{(2)} \) form of the cumulant depends only on the magnitude of the NO occupations, and removes the explicit dependence of the C3 correction (8.15) of \( c_{ij} \) on the type of NOs, thus permitting automatic calculation of \( c_{ij}^{AC3} \) within the self-consistent DMFT procedure. The results of the test calculations with the AC3 functional will be presented in the following section.

8.3 Comparative AC3 calculations of the potential energy curves

In this Section the results of comparative calculations of the potential energy curves with the approximate DMFT functionals PNOF0 (see Section 7.6), ML (see Section 7.7), and AC3 (see Section 8.2) are presented.

Figures 8.3-8.8 display the PNOF0, ML, and AC3 potential energy curves for the dissociation of the electron pair bond X-H in \( \text{H}_2 \), in the series of the ten-electron hydrides \( \text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{HF} \) as well as in HCN. The type of the bonds calculated range from the covalent electron pair bonds H-H and C-H to the strongly polar bonds O-H and F-H. The DMFT-AC3 calculations are performed according to the procedures of Refs. [96, 114]. A minimum is found in a two-step minimization procedure, in which the NOs are optimized (again iteratively) with fixed occupation numbers and then the occupation numbers are optimized. The occupation number optimizations are fast, but the NO optimization is relatively slow, scaling \( M^5 \) if \( M \) is the basis set size. For a correlated method the scaling is still quite acceptable.
Energy curves for the molecule H\textsubscript{2} calculated with the DMFT functionals ML, PNOF0, AC3, DFT functional BLYP, HF and FCI methods. The levels on the right hand side mark the sum of the energies of two individual H atoms calculated with unrestricted BLYP and unrestricted HF.
8.3. COMPARATIVE AC3 CALCULATIONS OF THE POTENTIAL ENERGY CURVES

Figure 8.4: Dissociation curve of CH$_4$

Energy curves for dissociation of a single C-H bond of CH$_4$, keeping the geometry of the CH$_3$ fragment fixed. Calculations with the DMFT functionals ML, PNOF0, AC3, DFT functional BLYP, HF and MRCI methods. The levels on the right-hand side mark the sum of the energies of the individual fragments H and CH$_3$ calculated with BLYP, HF and MRCI.
The reference curves are those of the full CI (FCI) for H₂ and of MRCI for the other molecules calculated with the GAMESS-UK package [115]. As a natural reference, the curves of the restricted HF method are also included as well as those of the standard functional of Becke-Lee-Yang-Parr (BLYP) [64, 116] of DFT. For the DFT-BLYP calculations the DALTON package [117] is employed. Calculations are performed in the correlation-consistent polarized cc-pVTZ basis set for all atoms [81]. For heavier atoms C, N, O, F the f-function and the most diffuse d-function are excluded from the basis. Since our primary goal is comparative calculations, the geometry of the dehydrogenated fragments is not optimized during dissociation and they are kept frozen at the equilibrium geometry of the intact molecule.

Figures 8.3-8.8 demonstrate a large difference between the reference FCI/MRCI curves and the restricted HF ones. This reflects the well-known HF error of too high (not sufficiently negative) electronic energies due to its neglect of electron correlation. This error increases significantly in the dissociation limit. It is somewhat less well known that the potential curves of the spin-restricted standard DFT functionals exhibit a similar dissociation limit deficiency [18], as can be clearly seen in Figure 8.3 for H₂. In this case BLYP reproduces the FCI curve near the equilibrium geometry, while at larger interatomic distances R(H-H) it makes the same qualitative error as HF. Though not to the same extent as HF, BLYP still substantially underestimates the strong non-dynamical left-right correlation in dissociating H₂. Clearly, the picture behind standard DFT functionals of an xc hole localized around the reference electron, which is fundamentally right if the reference electron is near one nucleus in the stretched H₂ system, still cannot take into account that the left-right correlation pushes the other electron as far away as the
8.3. COMPARATIVE AC3 CALCULATIONS OF THE POTENTIAL ENERGY CURVES

Figure 8.5: Dissociation curve of NH$_3$

Energy curves for dissociation of a single N-H bond of NH$_3$, keeping the geometry of the NH$_2$ fragment fixed. Calculations with the DMFT functionals ML, PNOF0, AC3, DFT functional BLYP, HF and MRCI methods. The levels on the right-hand side mark the sum of the energies of the individual fragments H and NH$_2$ calculated with BLYP, HF and MRCI.
Energy curves for dissociation of a single O-H bond of H$_2$O, keeping the geometry of the OH fragment fixed. Calculations with the DMFT functionals ML, PNOF0, AC3, DFT functional BLYP, HF and MRCI methods. The levels on the right-hand side mark the sum of the energies of the individual fragments H and OH calculated with BLYP, HF and MRCI.
other remote nucleus of the dissociating H$_2$ [18]. This left-right correlation error of GGA-DFT (BLYP) for H$_2$ can be estimated from the difference between the energy $E_{\text{BLYP}}^{\text{restr}}$ of the dissociated molecule calculated with the spin-restricted BLYP and the sum $E_{\text{frag}}^{\text{BLYP}}(\text{unrestr})$ of the energies of open-shell fragments calculated with the spin-unrestricted BLYP and depicted in Figures 8.3-8.7. In H$_2$ we have the special case that the restricted BLYP energy is close to the full-CI energy at $R_e$, and the spin-unrestricted BLYP energy of the H fragment is again close to the accurate energy of the H atom, so the difference between the asymptotic restricted BLYP energy and the asymptotic full-CI energy is just the left-right correlation error of BLYP. When BLYP is not close to the full-CI energy, as is the case for the other molecules, both at $R_e$ for the restricted BLYP and asymptotically for unrestricted BLYP, then the BLYP left-right correlation error follows just from the difference of asymptotic restricted BLYP calculation of the molecule and the unrestricted BLYP calculations on the fragments.

A well-known feature of CI is the strong dependence of its results on the basis set. For the two-electron H$_2$ the CI calculations in the chosen basis produce results, which are close to the basis set limit. However, for the ten-electron systems the present basis is a rather moderate one, though it is already one of the largest basis sets used in DMFT calculations. In turn, the DFT results are less basis set dependent. The absolute value of the total DFT energy (with an approximate functional) does not have the exact total energy as a lower bound, and the functionals are usually parameterized (as the BLYP used here) to effectively account for the dynamical electron correlation in atoms. Because of this, the BLYP curves for the ten-electron series go substantially lower than the reference MRCI ones (See Figures 8.4-8.8) over the whole R range, including the asymp-
Energy curves for the HF molecule calculated with the DMFT functionals ML, PNOF0, AC3, DFT functional BLYP, HF and MRCI methods. The levels on the right-hand side mark the sum of the energies of the individual atoms H and F calculated with BLYP, HF and MRCI.
Energy curves for dissociation of the H-C bond of the HCN molecule, keeping the geometry of CN fixed. Calculations with the DMFT functionals ML, PNOF0, AC3, HF and MRCI methods. The levels on the right-hand side mark the sum of the energies of the individual fragments H and CN calculated with HF and MRCI.
CHAPTER 8. THE AUTOMATIC VERSION OF C3

totic region. This does not mean much. The performance of the DFT functionals is usually not judged by the total energies, but just by the difference between atomic and molecular energies. In these cases (Figs 8.4-8.8) the asymptotic restricted BLYP error, as mentioned, cannot be judged from the difference between restricted BLYP and MRCI at the end point, but can be estimated from the difference between the end point of the restricted BLYP potential curve and the unrestricted energy. In all cases the spin-restricted BLYP produces an appreciable left-right correlation error, though it is usually somewhat smaller than the above mentioned error in the case of $H_2$ (however, the limiting value on the restricted BLYP curve has not always been reached in the figures).

An interesting finding of this Chapter is that, just as restricted HF and restricted BLYP, the DMFT functionals PNOF0 and ML consistently underestimate the relative stability of stretched molecules. Due to this, the PNOF0 and ML curves exhibit much larger deviations from the FCI/MRCI curves in the dissociation region while near equilibrium they go relatively closer to FCI/MRCI (See Figures 8.3-8.8). For the dissociating $H_2$ the PNOF0 error and the (larger) ML error are both rather close to the large HF error. Also for the ten-electron hydrides and HCN the upward shift of the PNOF0 and ML curves in the dissociation region is clear, and the corresponding absolute deviations remain large (See Figures 8.4-8.8). For the largest distances in the figures (which correspond to the asymptotic energies for MRCI and AC3, but clearly do not yet represent the dissociation limit for BLYP, PNOF0 and ML curves) the lower bound to the ML error ranges from ca. 0.1 Hartree for HF and CH$_4$ to 0.14 Hartree for NH$_3$, while the somewhat smaller (lower bound to the) PNOF0 error ranges from 0.07 Hartree for HCN to 0.1 Hartree for NH$_3$. In the case of PNOF0 the asymptotic error origi-
nates from the disregard in this functional of the strong-correlation situations, where NO occupations may tend to 1.0. The PNOF0 functional applies out of the set of C3 corrections only the third entry in Equation (8.14), but without the precaution of C3 of excluding from that correction the orbitals with occupations tending to 1.0 (the “bonding” and “antibonding” ones). This implies application of the full diagonal GU correction, which results in the neglect of the diagonal two-electron cumulant throughout, also for the bonding and antibonding NOs. As was argued in Ref. [13], this neglect destroys the asymptotically correct Heitler-London description of the left-right correlation and it leads to a substantial underestimation of stability of the dissociating molecules.

The ML functional is a total modification of the CH functional. The exchange term in Equation (8.5) is canceled, and the whole exchange-correlation energy is then represented with the second term in Equation (7.15) replacing \(-\sqrt{n_i n_j}\). The parameter optimization for the ML functional used the equilibrium geometries of a subset of the G2 set of molecules, and therefore did not probe strong correlation cases with occupation numbers close to 1.0. In the systems with only dynamical correlation (closed shell molecules at \(R_e\)) studied by ML only occupation number ranges occur close to 2.0 (or 1.0 in the scale 0.0-1.0 used by ML) and close to 0.0, see Fig. 2 of Ref. [59]. The ML functional achieves very good correlation energies at \(R_e\) for molecules with these occupation number ranges. For high occupation numbers the ML functional is smaller than the CH functional, leading to less negative energies. The same effect is achieved with the C2 correction, see discussion in Ref. [13] for the effect of this correction for the strongly occupied orbitals. For small occupation numbers the ML functional, for most of the \(n_i n_j\) values that occur, appears to be larger than the CH functional (more stabilizing). The empirical parameter fitting obviously is able to
strike a good balance between these positive and negative effects, so that the net effect is less stabilization than the (overcorrelating) CH functional. However, the ML functional appears to fall short of the $-\sqrt{n_i n_j K_{ij}} \approx -K_{ij}$ stabilizing contribution which is appropriate in the dissociation limit when $n_i \approx n_j \approx 1.0$. At this point the ML functional, being in that region linear in $\frac{1}{2} n_i n_j$, see Fig. 1 of Ref. [59], obtains only $-\frac{1}{2} K_{ij}$. This error is made for the diagonal terms with $c_{ii}^{ML}$, $i = a, b$, and the offdiagonal $c_{ab}^{ML}$ term. This is presumably the reason that the energy of the ML curves goes rather too high (not stabilizing enough) in the dissociation region. So it appears that it is the neglect of the strong non-dynamical correlation situations in both the ML and PNOF0 functionals that lead to the large errors of these functionals at long bond distances.

C3 and AC3 have been constructed with the aim to yield good correlation energies also in regions where interactions between atoms become weak and the (nondynamical) correlation becomes large. It is gratifying that the AC3 curves are fulfilling the expectations. The AC3 reproduces well the full reference MRCI potential curves for the ten-electron series and HCN (See Figures 8.4 - 8.8). The best AC3 case appears to be $\text{H}_2\text{O}$, for which the AC3 curve coincides (on the scale of Figure 8.6) with the MRCI one both around the equilibrium distance and in the dissociation limit, while the only visible discrepancy between the curves occurs in the intermediate region $3 \text{ Bohr} < R(\text{O-H}) < 5 \text{ Bohr}$. This trend holds also for other ten-electron hydrides and HCN. There is, however, a serious deficiency in the curve for $\text{H}_2$. Around 3.75 Bohr there is a spurious maximum in the AC3 curve, and at distances larger than 2 Bohr it already starts to deviate considerably from the full CI curve. It is actually rather close between 2 and 3 Bohr to the PNOF0 and
8.3. COMPARATIVE AC3 CALCULATIONS OF THE POTENTIAL ENERGY CURVES

ML curves, but it turns down to the correct asymptotic behavior too late, so that the mentioned maximum appears. Further optimization of the AC3 functional will need to address this point by considering more flexible, possibly asymmetrical damping factors.

Considering now the behavior of the various functionals around R_e, we note that in this small sample of molecules AC3 appears to be closest to the reference MRCI curves: for the ten-electron hydrides the PNOF0 and ML curves appear to bracket the AC3 curve, PNOF0 being too high and ML too low for CH_4, H_2O, NH_3 and HF. At R_e AC3 is closest to the benchmark MRCI result for CH_4, NH_3, H_2O and HF, but for HCN PNOF0 is the closest, ML and AC3 having a very similar slightly larger deviation. HCN is the only case where the AC3 shows a small but clear deviation towards stronger bonding with respect to the MRCI curve for a long range of intermediate distances (2.5 – 6 Bohr). In order to quantify the behavior around R_e somewhat better, we present in Table 8.1 the DMFT and FCI/MRCI total energies E_{tot} and correlation energies E_{c}, calculated at the equilibrium geometry. H_2 is special, it is the only case where all DMFT functionals appreciably underestimate the correlation, for AC3 and PNOF0 with large percentages (23% and 41% respectively). In all many-electron system the BB functional, using only J and K integrals leads to computational expense similar to Hartree-Fock. The correction that are added, however, use specific integrals over the NOs, making as the errors are small. For the ten-electron hydrides and HCN ML consistently overestimates correlation, PNOF0 consistently underestimates it, while AC3 produces errors of either sign, with the average absolute error of AC3 (3.3%) being about twice as small as the ML (6.7%) and PNOF0 (6.9%) errors. Since our set of molecules is small, we can only draw a very tentative conclusion from this comparison. It
is notable that the extensive benchmarking performed by Lathiotakis and Marques in Ref. [58], which did not yet include the ML functional, has yielded very similar quality for the C3 and PNOF0 functionals. Very recently Marques and Lathiotakis [59] showed that the ML functional performed on average better for the correlation energies at $R_e$ over the G2 set. The average error of 3.3% in our small sample is lower than either the ML result (11%) or the C3 result (18%) of Ref. [59] over the whole G2 set. This may just be accidental, it may also be due to the fact that we use larger basis sets or the AC3 results may be a bit better than the C3 functional tested by Marques and Lathiotakis.

Table 8.2 compares the equilibrium bond distances $R_e(X-H)$ calculated with the HF, FCI/MRCI, ML, PNOF0, AC3, and BLYP with the corresponding experimental values. Among the reference methods, HF produces the shortest bonds in all cases (except for CH$_4$ and HCN). CI yields, on average, longer bonds, while the experimental $R_e$ values are still larger and BLYP produces the longest bonds, typically 0.01 – 0.03 Bohr longer even than experiment. Among the DMFT functionals, ML produces the shortest bonds, while AC3 yields the best correspondence with CI. Indeed, for H$_2$O and HF AC3 reproduces the CI values with all three digits, while for NH3 the corresponding difference is only 0.001 Bohr (See Table 8.2).

### 8.4 Conclusions

In this Chapter a density matrix functional is proposed which employs only Coulomb and exchange integrals, with an automatic (occupation number driven) calculation of the expressions for the $\Gamma_{zc,ijji}$ elements of the exchange-correlation part of the two-density,
### 8.4. CONCLUSIONS

**Table 8.1:** Comparison of the ML, PNOF0, and AC3 and MRCI total energies ($E_{\text{tot}}$) and correlation energies ($E_c$) in Bohr for the equilibrium geometry

<table>
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<tr>
<th></th>
<th>H$_2$</th>
<th>CH$_4$</th>
<th>NH$_3$</th>
<th>H$_2$O</th>
<th>HF</th>
<th>HCN</th>
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<td><strong>PNOF0</strong></td>
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</tr>
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</table>

Error (%)

- HF: 23.1 7.4 -1.7 0.0 1.3 -5.9
- CI: 41 11.1 6.8 7.3 6.4 2.8
Table 8.2: Comparison of the calculated equilibrium bond distances in Bohr

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<th>NH₃</th>
<th>H₂O</th>
<th>HF</th>
<th>HCN</th>
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<td>1.888</td>
<td>1.777</td>
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<td>1.403</td>
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</tr>
<tr>
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<td>1.789</td>
<td>1.704</td>
<td>1.978</td>
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which lead to “exchange-like” matrix elements. Previously, in the C3 functional, the effects of strong (nondynamical) correlation had been taken care of by selecting manually the NOs involved in the strong correlation (having occupations tending to 1.0). We have presented this functional in a slightly different way (without changing the physics) by casting it in the form of a modeling of the two-electron cumulant. Since we have based ourselves from the beginning on the so-called C1 correction to the CH functional we effectively start from a functional that is exact for prototypical two-electron cases. This functional can be obtained from the work of Löwdin and Shull for two-electron systems [48]. While incorporating all the C3 corrections to the CH functional [13], which entered the previously proposed C3 functional, AC3 has the advantage over the latter that no manual selection of NOs involved in strong correlation (bonding and antibonding NOs in the present case) is required in AC3. From the comparisons to other success-
ful functionals we have noted that the proper treatment of strong correlation cases is crucial in order to obtain physically meaningful full potential energy curves. For instance we note that the PNOF0 functional, which uses a subset of the C3 corrections, but lacks the special treatment of strong correlation included in AC3, is competitive with AC3 around the equilibrium bond length, also for the magnitude of the errors in the correlation energy, but fails to describe the large-R region. In the present small sample of molecules the average absolute error of the correlation energies is lowest for AC3 (for the ten-electron systems it is only 3.3%). AC3 also reproduces very well the equilibrium bond distances for the ten-electron series. For H₂ AC3 is free of the large HF and BLYP dissociation limit errors, but the energy curve exhibits a spurious maximum, and the correlation energy is relatively poor (23 % error).

One can conclude, that AC3 correctly reproduces the electron exchange and both dynamical and non-dynamical correlation for the investigated systems which, besides the equilibrium or stretched electron pair bond, possess also other unbroken bonds as well as core electrons and electron lone pairs. This has been achieved with JK-only (primitive) functionals of the NOs and the NO occupations. The non-locality of these functionals, which is inherent in the use of the delocalized NOs, is presumably an important factor in their improvement over pure DFT functionals in the weak interaction region. The present functional has few parameters, which have been determined from a very limited number (4) of benchmark calculations. It is remarkable that the AC3 functional, without further optimization, achieves similar or even better quality of potential energy curves than its rigid C3 predecessor in spite of the fact that the dependence on occupation number and type of orbital is after parameter optimization somewhat different from C3 (the complete
suppression of some terms is replaced by reduction to ca. 30%). Probably this signifies that there is considerable leeway in the parameter determination. This may turn out to be rather important when further parameter optimization is carried out to improve the H$_2$ curve along with a larger set of benchmark molecules and covering many more cases of interest (notably multiply bonded systems, open shell systems, transition states, etc.) in a comprehensive density matrix functional. Preliminary AC3 calculations of the potential energy curve of the double-bonded C$_2$H$_4$ show promising results, while for the triple-bonded N$_2$ special precautions may be needed to ensure symmetry-equivalence (equal occupation numbers!) of the $\pi_x$ and $\pi_y$ orbitals, as is effectively done in Ref. [59] in the successful application of C3 to multiply bonded systems.

We consider it a great advantage of the DMFT functionals that it is very clear in what way the physics of electron correlation is modeled, and which types of correlation are treated. Apart from the dynamical correlation (relevant at R$_e$ for “normal” molecules) and the strong nondynamical correlation at bond breaking, which seem to be amenable by treatment with JK-only functionals, also Van der Waals interactions can be analyzed and incorporated [109]. That very different type of correlation would require in principle non-JK terms in the cumulant, although about half of the van der Waals energy has been obtained with a JK-only functional [118].
Part III

Conclusions, Outlook and Summary

Before I came here, I was confused.
Having listened to your lecture I am still confused.
But on a higher level.

(Enrico Fermi)
Motivation of Orbital Dependent Functionals
Quantum Chemistry makes large contributions to science. The accurate description of electron correlation is the main goal. The interaction of matter on the molecular scale is then predictable. In addition, molecular properties can be derived. Orbital Dependent Functionals provide the latest step towards an accurate description of electron correlation and molecular properties.

Shortcomings of DFT
In DFT two shortcomings can be identified. On the one hand there are difficulties to account for static correlation. This results in an inaccurate description of forming and breaking of a chemical bond. The H₂ dissociation curve stands as an example for this failure. On the other hand response properties are calculated incorrectly. The band gap of semiconductors and the excitation spectrum of molecules are deficient. The inaccurate description of static correlation is addressed to the energy functional. One of the origins of wrong response properties and excitation spectra is the inaccurate local potential. It is believed that Orbital Dependent Functionals should provide a remedy to both [8, 9, 10, 11, 12]. This work shows, however, that an improved total energy is not expected from avail-
able Orbital Dependent Functionals. Moreover, it is argued that potentials derived from Orbital Dependent Functionals are deficient.

Conclusions of Part I
In Part I of this work Orbital Dependent Functionals in Density Functional Theory are investigated. None of the available Orbital Dependent Functionals improve upon current density functionals. The Exact Exchange Functional (EXX) gives worse energies than Hartree Fock, which itself is incapable of describing correlation effects. The class of functionals based on perturbation theory fails to describe static correlation. The orbital energy differences in the denominator lead to a breakdown of the total energy in the dissociation limit of $H_2$. In Chapters 3 and 5 it is demonstrated that this can happen even for typical dynamical correlations systems, like He and Ne.

Finally, it is shown, that the Corrected Hartree Functional with $\epsilon_i$ dependence (CH-$\epsilon$) gives unphysical results if the the orbital energy is used to regulate involvement of the virtual orbitals. Too low virtual orbital energies are obtained, even if a balanced potential basis is used. It is argued that virtual orbitals should enter all parts of the energy functional. This leaves Density Matrix Functional Theory (DMFT) as an obvious next step.

A criticism of finite basis OEP
Orbital Dependent Functionals in DFT are closely connected to the Optimized Effective Potential (OEP). In this work it has been shown that a unique solution exists in a complete basis set. The OEP yields the minimum total energy with a unique potential. From this analysis it is straight forward to believe that OEP is a valuable tool for Orbital Dependent Functionals in DFT.

However, with a finite orbital basis difficulties arise. In Chapters
3 and 4 it was shown that (infinitely) many potentials exist, that all yield the minimum total energy. Thus, a unique orbital spectrum is not available. Different schemes have been proposed to cure this problem. All schemes [30, 31, 42, 43, 44] make a judicious choice about the potential basis. For a given (large) orbital basis the potential basis is truncated till the obtained results agree with complete orbital basis calculations. This “stop-when-convenient” approach is unsatisfactory. Moreover, the total energies that are obtained with different balancing schemes deviate significantly. Discrepancies of ca. 1 mH are already found in simple cases like CO [42, 44, 45] and N$_2$ [43, 44].

**Introduction to DMFT**

In Part I it is advocated to use Orbital Dependent Functionals with virtual orbitals entering all parts of the energy functional. An obvious next choice is the use of Orbital Dependent Functionals in Density Matrix Functional Theory (DMFT). Only a few functionals are available. There is still a great need for more accurate functionals.

**Short summary Part II**

In Part II Orbital Dependent Functionals in DMFT are investigated. The most advanced functional [53] depends on a preselection of bonding and anti-bonding orbitals. Chapter 8 presents the results for an automatic version of this functional. Excellent results for the dissociation curve of small benchmark molecules are obtained. Both dynamical and static correlation is excellently reproduced.

**Conclusions of Chapter 3**

In Part I problems of finite orbital basis sets in Optimized Effective Potential methods are isolated. A remedy is proposed and applied
to the problematic cases. It is proven that only some of the problems must be ascribed to the basis set. It is concluded that virtual orbitals should enter all parts of the energy functional.

In Chapter 3 calculations on CH-ɛ with large potential basis sets and, consequently, large variational freedom are performed. Too flexible potential basis sets might lead to disastrous total energies. In reference [40] it is shown that the exact exchange energy minimum in a finite orbital basis actually coincides with the HF energy.

A key feature of Kohn Sham Density Functional Theory is that both occupied and unoccupied orbitals feel the same local potential. Hence, with large variational freedom in the potential basis the Optimized Effective Potential energy minimization (2.51) might lead to vanishing gap of highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO). A numerical example for the He atom is given in Section 3.1.

A vanishing gap between HOMO and LUMO is particularly disastrous for the Görling-Levy second order perturbation theory functional (GLPT2). The energy difference between HOMO and LUMO is contained in the GLPT2 energy definition (2.43). It enters in the denominator. This leads to a variational collapse of the total energy. In Section 3.2 this is shown even for the He atom, which until now stood out as a “safe” simple case [11].

A particular version of the non-perturbative Corrected Hartree functional ɛ; with dependence (CH-ɛ) is considered in Section 3.3. A Fermi-type distribution is used to calculate the fictitious occupation numbers. The HOMO-LUMO gap is used to regulate the involvement of the virtual orbitals. It is proven, that the total energy breaks down in the He case. In particular, it is noted that the involvement of virtual orbitals only in the exchange correlation energy leads to the breakdown.
Conclusions of Chapter 4

Chapter 4 is a first contribution to the efforts [23, 30, 31, 42, 43, 45] to cure the problems of finite basis set Optimized Effective Potential methods. The correct total energy for the exact exchange functional is restored. However, the orbital energies still show instabilities. They depend on the reference potential $v_0(r)$ used in the direct optimization scheme (2.68).

The interdependence of orbital and potential basis set is analyzed in Section 4.2. The correct total energy minimum of the exact exchange functional is reproduced with a balanced basis set. In order to reproduce the correct energy with full numerical precision, at least the same quality basis sets are required for the orbitals and the potential. However, to reproduce the energy in a given basis set with a physically meaningful accuracy a smaller basis for the potential is sufficient.

A serious problem of Optimized Effective Potential methods is the reliability of the calculated orbital energies. Imposing the HOMO condition reduces the variation in orbital energies. However, as is shown in Section 4.3, the accuracy of other orbital energies is, typically, many orders of magnitude lower than that for the total energies. The best accuracy is obtained with a reference potential $v_0(r)$ that enforces the correct asymptotic behavior of the potential.

Conclusions of Chapter 5

In Chapter 5 balanced basis sets of Reference [42] are employed for CH-ε. For Be the orbital basis is extended to include p functions. The charge density condition is imposed on the potential. It must stem from a charge density that integrates to N-1. The analogue of Koopmans’ theorem is enforced. The HOMO energy must equal the negative ionization potential.
CHAPTER 9. CONCLUSIONS

In Section 5.2 results for Be and Ne are presented. Reasonable total energies are obtained. The Optimized Effective Potential for Be is smooth and well behaved. In the case of Ne oscillations are observed. They are smaller than those presented in Chapter 3. This is a consequence of the balanced basis sets. However, the virtual orbital spectrum is desastrous. Degeneracy of HOMO and LUMO is observed in both cases.

The unphysically low virtual orbital energies can be explained. Involvement of virtual orbitals depends on the energy difference to the occupied orbitals. Stronger involvement leads to a larger exchange correlation energy. While virtual orbitals lower the total energy through the xc functional, they do not raise the energy in the remaining parts of the energy functional. This is because only occupied orbitals enter the kinetic, nuclear-electron and Coulomb energy functionals.

Section 5.3 introduces a new functional in an ad-hoc fashion. The fictitious occupations as defined for CH-ε are included in all parts of the energy functional. A well behaved potential is obtained together with a finite HOMO-LUMO gap. The results support conclusions drawn in Chapter 3. Virtual orbitals should be included in all parts of the energy functional. However, virtual orbital energies are still too low. The reason is found in the dependence of the fictitious occupation numbers on the orbital energies. A more thorough investigation and a rigorous theoretical framework is needed. DMFT is an obvious choice to circumvent the problems established in Chapter 5.

Conclusions of Chapter 8

One can conclude, that AC3 correctly reproduces the electron exchange and both dynamical and non-dynamical correlation for the
investigated systems which, besides the equilibrium or stretched electron pair bond, possess also other unbroken bonds as well as core electrons and electron lone pairs. This has been achieved with JK-only (primitive) functionals of the NOs and the NO occupations. The non-locality of these functionals, which is inherent in the use of the delocalized NOs, is presumably an important factor in their improvement over pure DFT functionals in the weak interaction region. The present functional has few parameters, which have been determined from a very limited number (4) of benchmark calculations. It is remarkable that the AC3 functional, without further optimization, achieves similar or even better quality of potential energy curves than its rigid C3 predecessor in spite of the fact that the dependence on occupation number and type of orbital is after parameter optimization somewhat different from C3 (the complete suppression of some terms is replaced by reduction to ca. 30%). Probably this signifies that there is considerable leeway in the parameter determination. This may turn out to be rather important when further parameter optimization is carried out to improve the $H_2$ curve along with a larger set of benchmark molecules and covering many more cases of interest (notably multiply bonded systems, open shell systems, transition states, etc.) in a comprehensive density matrix functional.

We consider it a great advantage of the DMFT functionals that it is very clear in what way the physics of electron correlation is modeled, and which types of correlation are treated. Apart from the dynamical correlation (relevant at $R_e$ for “normal” molecules) and the strong nondynamical correlation at bond breaking, which seem to be amenable by treatment with JK-only functionals, also Van der Waals interactions can be analyzed and incorporated [109]. That very different type of correlation would require in principle
non-JK terms in the cumulant, although about half of the Van der Waals energy has been obtained with a JK-only functional [118].
With the results of this work many open questions have been settled. Nevertheless, there are many questions that are left unanswered. This is common in science as is implied by the quote above.

**Functional Development in DFT**

In this work it has been shown that the Görling-Levy second order perturbation theory functional (GLPT2) and the Corrected Hartree functional with \( \epsilon \) dependence (CH-\( \epsilon \)) do not produce accurate results. Both functionals suffer from the possibility to construct a potential that makes the highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO) degenerate. Recently, a new set of functionals based on perturbation theory has been proposed [74]. These functionals are variationally stable in the complete basis set limit. Reference [119] proves variational stability for one of these functionals with finite orbital sets.

Functional development can also take a route away from established functionals [9] like generalized gradient approximations (GGA) and perturbation theory based functionals. The CH-\( \epsilon \) functional provides a first step on this endeavor. The new functionals must include virtual orbitals. It is now the task to develop schemes to regulate involvement of virtual orbitals. The new schemes should
CHAPTER 10. OUTLOOK

not depend on the orbital energies since this would most likely lead again to too low virtual orbital energies.

Finite basis set Optimized Effective Potential Methods
Various methods to solve the Optimized Effective Potential (OEP) equations have been proposed [23, 30, 31, 42, 43]. However, the solutions don’t seem to be unique. Different methods yield different results already for simple cases like CO [42, 44, 45] and N$_2$ [43, 44]. It remains to show that the differences are small even for larger systems (compare Table III of Reference [45]). Possibly one can still come up with a method that uniquely solves the OEP equations in a finite basis set.

Functional development in DMFT
In this work a new functional in DMFT has been proposed. It was tested only for small molecules. An efficient implementation of DMFT has still to be done. This will allow to test the available functionals on a greater set of molecules. Most likely it will be found that there is still room for improvement. In particular, it is expected that the parameters can still be optimized. Moreover, it is desirable to develop functionals that have a less complicated dependence on the natural occupation numbers.

Local-DMFT
It has become popular to combine different methods to obtain better functionals [12, 120, 121]. The author believes that a combination of DFT and DMFT much like the recently proposed \textit{ab initio} DFT [12] should give good results. DMFT functionals are minimized with a local potential, as was done in Section 5.3. The new methods
will be called Local-DMFT. Well behaved potentials are expected, because virtual orbitals enter all parts of the energy functional. Too low virtual orbital energies should not be observed. The obtained local potential can be used to calculate molecular response properties. Local-DMFT is expected to perform better than \textit{ab initio} DFT for dissociation curves because excellent DMFT functionals are available.
Summary

Short Summary of this work
Orbital Dependent Functionals in Density Functional Theory (DFT) do not yield reliable results. Both, the total energy as well as the response properties, cannot be uniquely determined. In DFT accurate response properties are obtained from the statistical averaging of (different) orbital potentials (SAOP) [87] and the gradient-regulated asymptotic correction (GRAC) [88].

In this work Orbital Dependent Functionals are used in Density Matrix Functional Theory (DMFT). An automatic version of the most advanced functional in DMFT [13] is presented. Excellent performance on the dissociation curve of small benchmark molecules is found. Both static and dynamical correlation is excellently reproduced. In DMFT response properties can be calculated from the recently developed time-dependent DMFT.

Summary of Chapter 3
In Part I of this work difficulties of Orbital Dependent Functionals in DFT are pointed out. Chapter 3 presents unphysical results for the Corrected Hartree Functional with $\varepsilon_i$ dependence (CH-\(\varepsilon_i\)) similarly to the ones found in the literature for the Exact Exchange
CHAPTER 11. SUMMARY

Functional (EXX) [40]. The total energy breaks down. The potential shows large oscillations. Degeneracy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO) is found.

Summary of Chapter 4
Chapter 4 presents a first step towards obtaining reliable results for EXX. The orbital basis and potential basis must be balanced. It is sufficient to use a smaller basis for the potential than for the orbitals. With a judicious choice for the reference potential an accurate orbital spectrum is obtained. More elaborate schemes have been proposed [23, 30, 31, 42].

Summary of Chapter 5
In Chapter 5 the balancing scheme of Reference [42] is employed for calculations on CH-ε. The charge density condition and the analog of Koopmans’ theorem are enforced. The results improve dramatically compared to Chapter 3. The total energy does not break down. However, the virtual orbital energies are too low. The LUMO energy is so low that it becomes degenerate with the HOMO energy. It is suggested that virtual orbitals should be included in all parts of the energy functional and not only in the exchange correlation term.

Summary of Chapter 8
An obvious next step is taken in Chapter 8. It deals with Orbital Dependent Functionals in DMFT. Energy functionals in DMFT naturally include virtual orbitals in all parts of the functional. Recently, a functional has been proposed which excellently reproduces
dynamical and static correlation. This is shown for the dissociation curve of small benchmark molecules [13]. A preselection of bonding and anti-bonding orbitals is the major downside of the functional. In Chapter 8 an automatic version is proposed. Excellent dissociation curves for a set of small molecules are obtained.
Samenvatting

Een Korte Samenvatting van deze proefschrift

Orbitaalafhankelijke functionalen in dichtheidsfunctionaaltheorie (DFT) geven onbetrouwbare resultaten. Zowel de totale energie als de responseigenschappen zijn niet eenduidig. Goede responseigenschappen zijn in DFT verkrijgbaar door het statistisch middelen van (verschillende) orbtaal afhankelijke potentialen (SAOP) [87] en door de gradiënt gereguleerde asymptotische correctie (GRAC) [88].


Samenvatting van Hoofdstuk 3

In deel I van dit werk worden de problemen met orbitaalafhankelijke functionalen in DFT uiteengezet. In hoofdstuk 3 worden de
onfysische resultaten voor de gecorrigeerde Hartree functionaal met $\varepsilon_i$ (CH-$\varepsilon$) gepresenteerd, welke vergelijkbaar zijn met de resultaten voor de exact exchange functionaal (EXX) uit de literatuur [40]: de totale energie is onbegrensd, de potentiaal vertoont sterke oscillaties en de hoogst bezette moleculaire orbitaal (HOMO) en de laagst onbezette moleculaire orbitaal (LUMO) worden ontaard.

Samenvatting van Hoofdstuk 4

In hoofdstuk 4 worden de eerste stappen gezet om betrouwbare resultaten met de EXX functionaal te verkrijgen. De orbitalbasis en potentiaalbasis moeten met elkaar in balans zijn. Het blijkt voldoende om een kleinere potentiaalbasis te kiezen dan voor de orbitalen. Met een verstandige keuze voor de referentie potentiaal is het mogelijk een goed orbitalspectrum te krijgen. Meer complexe methoden zijn ook voorgesteld [23, 30, 31, 42].

Samenvatting van Hoofdstuk 5

In hoofdstuk 5 wordt de balanseermethode uit Referentie [42] gebruikt voor CH-$\varepsilon$ berekeningen. De ladingsdichtheidsconditie en het analoog van het Koopmans theorema worden opgelegd. De resultaten zijn een stuk beter dan die in hoofdstuk 3: de energie is nu van onderen begrensd. Echter, de virtuele orbitaalenergieën zijn te laag; de LUMO energie is zelfs zo laag dat deze ontaard is met de HOMO. Dit wijst erop dat de virtuele orbitalen in alle delen van de energiefunctioaal moeten voorkomen en niet alleen in het exchange-correlatie gedeelte.
Samenvatting van Hoofdstuk 8
Een logische volgende stap wordt gezet in hoofdstuk 8. In dit hoofdstuk worden orbitaalafhankelijke functionalen in DMFT behandeld. Energiefunctionalen in DMFT hebben op natuurlijke wijze de virtuele orbitalen in elk gedeelte van de functionaal. Recent is een functionaal voorgesteld die de dynamische én statische correlatie zeer goed reproduceert. In het bijzonder voor de disso- ciatie van kleine ijkingsmoleculen [13]. Het grote nadeel van deze functiaanl is dat er vooraf een opdeling tussen bindende en anti- bindende orbitalen gemaakt moet worden. In hoofdstuk 8 wordt een geautomatiseerde versie voorgesteld. Uitstekende grondtoes- tandsenergieën voor een set kleine moleculen voor de gehele disso- ciatie worden met deze functionaal verkregen.
Zusammenfassung

Kurze Zusammenfassung dieser Arbeit
Verläßliche Resultate können von orbitalabhängigen Funktionalen in Dichte Funktional Theory (DFT) nicht erwartet werden. Sowohl die Gesamtenergie als auch die Resonanzeigenschaften können nicht eindeutig bestimmt werden. Innerhalb der DFT sind genaue Resonanzeigenschaften von dem statistischen Mittel der (unterschiedlichen) Orbitalpotentialen (SAOP) [87] und der gradientenregulierten asymptotischen Korrektur (GRAC) [88] zu erwarten.


Zusammenfassung des 3. Kapitels
In Teil I dieser Arbeit werden Schwierigkeiten von orbitalabhängigen Funktionalen in der DFT herausgestellt. In Kapitel 3 werden
unphysikalische Resultate für das Corrected Hartree Funktional mit \( \varepsilon \); Abhängigkeit (CH-\( \varepsilon \)) gezeigt. Diese sind denen ähnl ich, die in der Literatur für das exacte Austauschfunktional (EXX) gefunden wurden [40]. Die Gesamtenergie von (CH-\( \varepsilon \)) bricht zusammen. Das Potential weist starke Oszillationen auf. Entartung des höchsten besetzten Molekuelorbitals (HOMO) mit dem niedrigsten unbesetzten Molekuelorbital (LUMO) wird gefunden.

Zusammenfassung des 4. Kapitels


Zusammenfassung des 5. Kapitels

**Zusammenfassung des 8. Kapitels**

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