Thesis for the degree of Teknologie licentiat

Subsystem Functionals in Density Functional Theory

Towards a New Class of Exchange-Correlation Functionals

Rickard Armiento

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Cover illustration: An expression describing how the Mathieu gas density deviates from a uniform electron density for the z-point where the density gradient is zero, as a function of two parameters, $\bar{p}$ and $\sqrt{\bar{p}^2\bar{\lambda}}$.

Abstract

This thesis presents results relevant to the development of improved methods for theoretical calculations of properties of materials, molecules and atoms. The work is performed within the theoretical framework of the density functional theory, and is aimed towards new approximations of the exchange-correlation energy per particle, i.e., new 'functionals'. Two main contributions are given in this area: a) results and requirements for using approximations based on different starting points in different parts of a system, i.e., subsystem functionals, b) properties important for a starting point of a subsystem functional aimed at interior-like regions with slowly varying electron densities. A main result of the investigation is that the exchange energy per particle cannot be modeled with an ordinary (analytical) power expansion.

Key words: density functional theory, exchange energy, exchange-correlation functional, subsystem functional, Mathieu gas model.

Sammanfattning

Detta arbete presenterar resultat inom utvecklandet av nya metoder för teoretiska beräkningar av egenskaper hos material, molekyler och atomer. Arbetet är utfört inom området täthetsfunktionalsteori och är inriktat mot nya approximationer av utbytes-korrelationsenergi per partikel, d.v.s. nya "funktionaler". Två huvudsakliga vetenskapliga bidrag ges inom detta område: a) beskrivningar av resultat kring, och krav på, användandet av approximationer baserade på olika grunder i olika delar av ett och samma system, s. k. subsystemfunktionaler, b) resultat viktiga för grunden till en subsystemfunktional för inner-regioner med långsamt varierande elektrondensitet. Ett av arbetets huvudresultat är att utbytesenergin per elektron inte kan beskrivas av en vanlig (analytisk) serieutveckling.

Nyckelord: täthetsfunktionalsteori, utbytesenergi, utbytes-korrelationsfunktional, subsystemfunktional, Mathieugasmodell.

Preface

This thesis describes scientific work for the degree of Teknologie licentiat carried out in the group of Theory of Materials at the Department of Physics, Royal Institute of Technology. The work is a part of a very large ongoing effort: the development of improved methods for electron density functionals to be used in density functional theory (DFT) calculations. The main part of the time spent on this project has been used to develop a trustworthy and sufficiently optimized computer program for calculations on a quantum mechanical model system, which has been used to investigate properties of DFT quantities. Apart from the results obtained by using this program, efforts have also been made to carefully document the main construction of the program (this documentation is placed in the appendices of the paper in part II of the thesis). In addition, since the main results are argued from unanticipated numerical data, a clear description of the data treatment and a careful error analysis have been necessary to make the results convincing.

The thesis begins with a brief and general introduction to density functional theory in chapter 2 and 3. Chapter 4 presents the ideas of the subsystem functional approach towards improved DFT functionals. This is followed, in chapter 5, by an introductory treatment of the Mathieu gas model system, which is used as a model system for obtaining the data results of the thesis, modeling the behavior of DFT quantities. Chapter 6 investigates the power expansion of the kinetic energy density by using numerical data from the Mathieu gas model system. Finally, chapter 7 briefly discusses the purpose and contents of the paper comprising part II of the thesis.

The paper in part II has the title "Subsystem functionals in density functional theory: Investigating the exchange energy per particle". All data presented there were calculated by me, using a program written by me (although Ann Mattsson had performed some preliminary computations and her results provided a starting point). The data analysis and the writing of the main part of the paper were done jointly with Ann Mattsson, but the appendices were written by me.

Contents

Thread carefully, here there be monsters.

A traditional warning on old maps,
designating unexplored territory.

Chapter 1

Introduction

Current theories in physics, most notably quantum mechanics, provide a mathematical description of the world on a very small scale. They describe matter as composed by particles and their interactions. So far, measurements on the physical world seem to agree very well with quantum mechanics and it is believed that enough of the physical world has been captured in the theory to make it possible to describe physical properties also on larger scales, by using descriptions involving more and more particles. However, when trying to construct and study such a larger scale quantum mechanical description, the mathematics becomes too complicated to solve exactly; investigations must be done by approximative methods.

The study of quantum mechanics through approximations has proven very successful and has turned into a means of deriving unknown properties of compounds and materials. As a result, a new branch of physics has developed which can be described as using computers to perform 'experiments' and 'measurements' upon the mathematical framework of quantum mechanics.

Density Functional Theory (DFT) is a formulation of quantum mechanics that utilizes a view of the particles known as electrons as a compound sea, focusing on the density of electrons as a fundamental property. This is opposed to so called wave-functional approaches that keep track of all individual electrons. The gain of DFT over the wave-functional approaches is that the density of electrons is a three-dimensional property, whereas the wave-function used to keep track of the electrons is of a dimensionality proportional to the number of electrons in the system (which usually is very large). The price paid for the comparably simpler DFT description is that it gives up the ability to describe certain properties of a system (most of which are related to the individual movement of electrons). However, for other properties the DFT formulation has been shown to be as fundamental[1] as a wave-functional based approach.

When the DFT formulation is transformed into a form[2] suitable for computer calculations, the most difficult quantum mechanical behavior of the sea of electrons is put into the *exchange-correlation energy functional*, E_{xc}. This is

Original Kohn and
Mattsson approach

Generalized idea

Edge

Interior

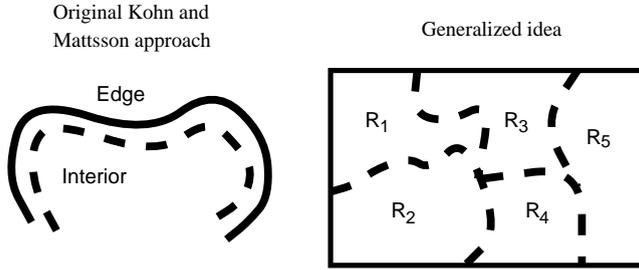R_1 R_3 R_5

R_2 R_4

Figure 1.1. The generalized idea of dividing a system into subsystems, applying different functionals to the different parts. The left figure refers to the approach presented by Kohn and Mattsson in Ref. 4.

usually a part of minor size, but it is the only part that has to be approximated relative to an explicit wave-functional solution. Several approximations of E_{xc} suitable for computer calculations have been developed, but there is a demand for even more accurate ones. This thesis presents work towards such improved approximations.

The main underlying idea of the work presented here is that a system can be split into several regions, and in each region a different way of approximating E_{xc} can be used. Each such approximation could then be specifically designed for the part of the system it is applied to. This is not possible if one and the same approximation is used throughout the whole system. The approach described here is based on the locality, or 'near-sightedness', of a system of electrons, which is a property that previously has been discussed in other works.[3,4] Kohn and Mattsson[4] have also presented efforts towards splitting a system into specific interior and edge parts. Hence, the present approach is based on a generalization of their ideas, as illustrated in Fig. 1.1.

The main scientific contributions of this thesis can be summarized as:

1. Establishment of fundamental results and requirements for using different approximations of E_{xc} in different parts of a system.

2. Investigation of properties of an approximation of E_{xc} useful for slowly varying electron densities.

1.1   Some Comments on Units

The form of certain equations depends on the choice of units in which they are expressed. This work uses SI units, but to avoid confusion because of the differing practices of units common in this field of physics, a brief summary of some unit systems follows.

Hartree atomic units

The bohr unit is introduced as a length based on quantities common for calculations on atomic scales. The hartree is then defined as the Coulomb repulsion between two electrons separated by one bohr.

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e_c^2} = 1 \text{ bohr}, \quad \frac{e_c^2}{4\pi\epsilon_0 a_0} = 1 \text{ hartree.} \tag{1.1}$$

But when speaking of hartree atomic units, one usually takes the hartree unit to be dimensionless (i.e., 1 hartree = 1) and additionally sets

$$\frac{\hbar^2}{2m_e} = \frac{1}{2}. \tag{1.2}$$

Some presentations stop here, because this is enough to get rid of the most common prefactors of quantum mechanical equations, simplifying them significantly. However, when numerical values are cited, it is not unusual also to make some other quantities dimensionless and equal to 1. Most commonly one lets $e_c = 1$, which equivalently makes $1/(4\pi\epsilon_0) = 1$. It is also common to additionally set $\hbar = 1$, which equivalently makes $m_e = 1$. After this last step, numerical values of quantities of other dimensions than energy and length are usually marked as given in "a.u.", designating atomic units, but giving the values with no unit at all is also formally correct.

Rydberg atomic units

The rydberg atomic units are based on the same ideas as the hartree atomic units but define the rydberg as the electron energy of the hydrogen atom

$$\frac{1}{2} \frac{m_e e_c^4}{(4\pi\epsilon_0)^2 \hbar^2} = 1 \text{ rydberg.} \tag{1.3}$$

It is found that 1 hartree = 2 rydberg. Within the rydberg atomic units one takes the rydberg to be dimensionless (i.e., 1 rydberg = 1) and also sets

$$\frac{\hbar^2}{2m_e} = 1. \tag{1.4}$$

As for hartree atomic units, some presentations stop here, but again it is common when citing values to also let other quantities be dimensionless and equal to one (usually the same quantities as for hartree atomic units).

SI and cgs units

The cgs and SI system of units are based on similar ideas within dimensions of mass, time and length but differ significantly in the area of electromagnetism. It exists at least two different conventions for the cgs system in this area, cgs-emu

and cgs-esu. In cgs-esu the charge unit has been chosen to simplify equations involving interactions between static electric charges by fixing the constant in Coulomb's law to one, giving $\epsilon_0 = 1/4\pi$. In cgs-emu the conventions are chosen to simplify equations involving moving charges by fixing the permeability of vacuum $\mu_0 = 1$ thus giving $\epsilon_0 = 1/c^2$. In general, when converting equations from the cgs systems to the SI system, one needs to insert carefully chosen constant factors as combinations of 4π, ϵ_0 and c (or $\mu_0 = 1/\epsilon_0 c^2$) for all electromagnetic variables present. The result of this conversion is, of course, dependent on the kind of cgs system one is working with, which, if unknown, usually must be determined by observing the appearance of a Coulomb factor in an equation where it is known that such a factor should appear.

Chapter 2

Density Functional Theory

Density functional theory (DFT) has already been briefly introduced in chapter 1. The main idea is to regard the total particle density as the primary quantity from which properties of the system can be obtained. This chapter begins with some fundamental concepts and then introduces the theoretical framework. For a more extensive treatment of density functional theory the reader is referred to text books on the subject.[5,6]

2.1 Background

The starting point is the time independent Schrödinger equation, which is the eigenvalue equation for the total energy operator, the Hamiltonian, $\hat{H}$. This equation implicitly defines all possible states, Ψ, of a system, and their related energies, E:

$$\hat{H}\Psi = E\Psi. \tag{2.1}$$

For electrons moving around positive-charged nuclei in the kind of systems we intend to treat here, it is common to assume that this equation can be separated into independent electronic and nuclei parts (this is the Born-Oppenheimer approximation,[7] valid when electrons can be said to enter equilibrium on a time scale sufficiently shorter than the time scale on which the nuclei move). This separates our states into independent states for nuclei, ϕ, and electrons ψ with respectively energies E_n and E_e. The Hamiltonian is split into corresponding terms, $\hat{H}_n$ and $\hat{H}_e$. We choose to put the interaction energy between nuclei and electrons into the electronic part. This gives

$$\Psi = \phi\psi, \quad \hat{H} = \hat{H}_n + \hat{H}_e, \tag{2.2}$$

$$\hat{H}_n\phi = E_n\phi, \quad \hat{H}_e\psi = E_e\psi. \tag{2.3}$$

Using this separation it is comparably easy to handle the nuclei part. Our efforts are thus directed towards the electronic part, which here can be seen as a system

of multiple interacting electrons moving in a static external potential created by the electric field of nuclei.

The energy operator of the electrons and electron-nuclei interaction, $\hat{H}_e$, is conventionally split into a sum of three contributions: the kinetic energy of the electrons, $\hat{T}$, the internal potential energy (the repulsion between the different electrons), $\hat{U}$, and finally the external potential energy (the attraction between the electrons and nuclei), $\hat{V}$. It is also common to use $\hat{F}$ for the total internal electronic energy, i.e., $\hat{T} + \hat{U}$:

$$\hat{H}_e = \hat{T} + \hat{U} + \hat{V} = \hat{F} + \hat{V}. \tag{2.4}$$

Let the location of electron i be denoted $\mathbf{r}_i$, the total number of electrons in the system N, and the potential energy field originating from the nuclei, in which the electrons are moving, $v(\mathbf{r})$. In a wave-function based description of the system electronic states, $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$, the contributions to the Hamiltonian become:

$$\hat{T} = -\left(\frac{\hbar^2}{2m_e}\right) \sum_{i=1}^{N} \nabla_i^2, \tag{2.5}$$

$$\hat{U} = \left(\frac{e_c^2}{4\pi\epsilon_0}\right) \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{2.6}$$

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i). \tag{2.7}$$

Taking the expectation value for the energy gives an explicit expression

$$E_e = \langle \psi | \hat{T} + \hat{U} + \hat{V} | \psi \rangle = T + U + V =$$
$$\iint \cdots \int \left(-\left(\frac{\hbar^2}{2m}\right) \sum_{i=1}^{N} \psi^* \nabla_i^2 \psi + \left(\frac{e_c^2}{4\pi\epsilon_0}\right) \sum_{i<j}^{N} \frac{|\psi|^2}{|\mathbf{r}_i - \mathbf{r}_j|} + $$
$$+ \sum_{i=1}^{N} |\psi|^2 v(\mathbf{r}_i) \right) d\mathbf{r}_1 d\mathbf{r}_2 ... d\mathbf{r}_N. \tag{2.8}$$

Here T, U and V are introduced as the individual, scalar, expectation values of the respective operators.

The expression for E_e can be simplified by introducing the electron density, $n(\mathbf{r})$. The relation between $n(\mathbf{r})$ and the wave function is

$$n(\mathbf{r}_1) = N \iint \cdots \int |\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)|^2 \, d\mathbf{r}_2 d\mathbf{r}_3 ... d\mathbf{r}_N. \tag{2.9}$$

The expression on the right hand side is similar to a wave function normalization expression, but with one of the integrals left out, i.e., leaving one index free. It

is not important which of the indices of the wave function is left out, as the electrons are indistinguishable, and a proper wave function must reflect this.

When looking at the three terms in the expression for the expectation value of the energy, Eq. (2.8), we see that only one term is easily rewritten in terms of the density, the term for the external potential, V:

$$V = \iint ... \int \sum_{i=1}^{N} v(\mathbf{r}_i) |\psi|^2 \, d\mathbf{r}_1 d\mathbf{r}_2 ... d\mathbf{r}_N =$$

$$= \frac{1}{N} \sum_{i=1}^{N} \int n(\mathbf{r}_i) v(\mathbf{r}_i) d\mathbf{r}_i = \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}. \qquad (2.10)$$

The other two terms in Eq. (2.8) cannot be rewritten in this simple way. In the kinetic energy term, T, the derivative operator between the wave functions makes it non-straightforward to put it into a 'density'-form with the two wave functions next to each other, and in the term of the internal potential energy, U, the two different particle locations present within the integrations prevent a simple term by term integration.

The dependencies found above can be stated in an explicit way using functionals:*

$$E_e = T[\psi] + U[\psi] + V[v, n] = F[\psi] + V[v, n]. \qquad (2.11)$$

This is just a simplified notation for the energy of a general electron wave function, i.e., Eq. (2.8). As indicated by the designation $F[\psi]$, that functional is independent of the external potential v.

A possible way of solving an electron energy problem is to search for the ψ that minimize E_e. This approach leads to wave-function based methods, i.e., methods that are based on finding a minimizing wave-function in a space of functions of a dimensionality proportional to the number of electrons in the system. In contrast, the DFT approach is to rewrite $F[\psi]$ so as to depend only on the electron density $n(\mathbf{r})$. Below it is shown how a minimization of the three-dimensional $n(\mathbf{r})$ constitutes an alternative way of solving the electron energy problem. The first thing to be considered is the existence of a $F[n]$ functional.

2.2 The Thomas–Fermi Model

Early attempts to approximate $F[\psi]$ in functionals of only the density were performed by Thomas and Fermi.[8, 9] Quantum mechanical calculations using

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*A functional is an object that acts on a function to produce a scalar. It is written as an ordinary function except that the function it acts on is placed within bracket parentheses, [ ]. For a good review on functionals, see Ref. 5

assumptions about the distribution and the interaction between electrons, give the following approximation for the kinetic energy:

$$T \approx T_{\text{TF}}[n] = \frac{3}{10}(3\pi^2)^{2/3}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\int n^{5/3}(\mathbf{r})d\mathbf{r}. \qquad (2.12)$$

A simplistic approximation of the internal potential energy, U, is given by the expression for a classically repulsive gas (i.e., completely ignoring the quantum interactions between electrons described by the Pauli principle):

$$U \approx J[n] = \frac{1}{2}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\iint\frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2. \qquad (2.13)$$

This gives the Thomas–Fermi model:

$$E_e \approx T_{\text{TF}}[n] + J[n] + \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \qquad (2.14)$$

The result is a first approximation of a $F[n]$ functional, i.e., $F[\psi] \approx T_{\text{TF}}[n]+J[n]$.

2.3   The Hohenberg–Kohn Theorems

The early efforts to find energy density functionals (the Thomas–Fermi model and extensions along the same idea) were all based on 'sensible' approximations which gave decent results when applied to certain real problems. There is a great conceptual difference between these heuristic 'guesses' and the elegant theoretical framework following the work of Hohenberg and Kohn[1] (HK).

The first of the two HK theorems tells us that the ground state electron density $n(\mathbf{r})$ determines the potential of a system, $v(\mathbf{r})$, within an additive constant (which only sets the absolute energy scale). The proof is outlined in the following. Assume two different system potentials, $v_a(\mathbf{r})$ and $v_b(\mathbf{r})$. They must, if they differ by more than an additive constant, give rise to two different ground states in the Schrödinger equation, ψ_a and ψ_b. Let us assume that the states are non-degenerate and that they give the same electronic density, $n(\mathbf{r})$. The quantum principle of variation gives (using $\hat{\text{H}}_a$ as the Hamiltonian for the system with potential $v_a(\mathbf{r})$)

$$E_a = \langle\psi_a|\hat{\text{H}}_a|\psi_a\rangle < \langle\psi_b|\hat{\text{H}}_a|\psi_b\rangle = F[\psi_b] + V[v_a, n], \qquad (2.15)$$

and consequently

$$E_b < F[\psi_a] + V[v_b, n]. \qquad (2.16)$$

Adding the two equations, and recollecting the terms, gives

$$E_a + E_b < E_b + E_a. \qquad (2.17)$$

This last relation is clearly a contradiction. The conclusion is that for systems without degenerate ground states, two different potentials cannot give the same

ground state electron density. This means that it is theoretically possible to obtain *all ground state properties of a system* from the ground state electron density, $n(\mathbf{r})$. Based on this, the ground state wave function can be considered as a functional of the ground state density $\psi[n]$, which proves the existence of an unapproximated energy functional, $E_e[n]$:

$$E_e[n] = \langle\, \psi[n]\, |\hat{H}_e|\, \psi[n]\, \rangle. \qquad (2.18)$$

Thus the electronic energy functional, $F[n]$, must also exist as a functional of the ground state electron density.

It was later shown[10–13] that it is possible to construct a (somewhat artificial) explicit definition of $F[n]$:

$$F[n] = \min_{\psi \to n} \langle\psi|\hat{T} + \hat{U}|\psi\rangle, \qquad (2.19)$$

where the minimum is taken over all ψ that give an electron density of n. This is commonly referred to as the *constrained search formulation*. In this form the DFT formalism does not require a non-degenerate ground state.

The second of the two Hohenberg–Kohn theorems provides a variational principle for the total energy combination[†] $F[n] + V[v, n]$. If we denote a trial density by $\tilde{n}(\mathbf{r})$, the quantum mechanical principle of variation directly gives:

$$F[\tilde{n}] + V[v, \tilde{n}] = \langle\, \psi[\tilde{n}]\, |\hat{H}_e|\, \psi[\tilde{n}]\, \rangle \geq \langle\, \psi[n]\, |\hat{H}_e|\, \psi[n]\, \rangle = F[n] + V[v, n], \quad (2.20)$$

where the minimum is known to occur only for:

$$\psi[\tilde{n}] = \psi[n] \quad \Rightarrow \quad \tilde{n} = n. \qquad (2.21)$$

The existence of this variational principle is the reason to why it is so useful to have an approximation of $F[n]$. Given a good enough approximation, the electronic energy can be obtained by what seems to be a rather uncomplicated minimization of a three dimensional function $n(\mathbf{r})$. Hence, we have found a method of handling the difficult part of Eq. (2.3).

In practice, however, complications do enter here, since the formal constrained search definition of $F[n]$, Eq. (2.19), is very complicated and actually returns the scheme to a minimization with respect to wave-functions of high

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[†]Note that the combination used here, $F[n] + V[v, n]$, is not equivalent to the $E_e[n]$ shown to exist in Eq. (2.18). The difference is that the latter uses the external potential that corresponds to the inserted trial density, whereas the former uses an explicit dependence on the real external potential of the actual system. It is possible to see the difference in formal terms by defining $E_e[n]$ as $F[n] + V[v(\mathbf{r}, [n]), n]$. A clarification to why this $E_e[n]$ cannot be used in a variational principle follows. Consider two different electron densities, $n(\mathbf{r})$ and $\tilde{n}(\mathbf{r})$. If n is the exact density and one uses $\tilde{n}$ as a trial density one expects the variational principle to give $E[\tilde{n}] > E[n]$, as all trial densities should give higher energies than the true density. But, in a different problem $\tilde{n}$ may be the exact density, and if one now happens to use n as a trial density, one would expect $E[\tilde{n}] < E[n]$. A variational principle for $F[n] + V[v, n]$ does not suffer from this problem, because the explicit dependence on the real external potential $v(\mathbf{r})$ differentiates between the two test cases.

order. It is not feasible to perform a constrained search in practice, because then nothing would be gained over traditional wave-function based methods. Instead, the above findings are just a formal establishment of the existence and possible use of a general $F[n]$, giving little or no hint on how to approximate it. Consequently, approximations of $F[n]$ must be constructed using more elaborate methods than simply 'just approximating the constrained search'.

Chapter 3

DFT Calculations

Having established the theoretical foundation of DFT, it is time to consider its practical use.

3.1 The Kohn–Sham Scheme

In 1965 it became clear how to turn the theoretical framework of density functional theory into a practical computational tool as Kohn and Sham[2] proposed a method for computing the most important part of the kinetic energy functional to good accuracy. The idea was to rewrite the problem of many interacting electrons to make it possible to use an analogue with a system of many *non-interacting* electrons.

The first step is to restructure the components of the functional $F[n]$ slightly, introducing T_s as the kinetic energy of a system of non-interacting electrons and $J[n]$ as it was defined in the section about Thomas–Fermi theory, Eq. (2.13):

$$F[n] = T_s[n] + J[n] + E_{xc}[n], \qquad (3.1)$$

where the *exchange correlation energy*, $E_{xc}[n]$ consequently is defined to make this relation exact, i.e.,

$$E_{xc}[n] = F[n] - T_s[n] - J[n]. \qquad (3.2)$$

This component of $F[n]$ does, in some sense, take care of the non-classical corrections to the energy, and is the only part for which approximations are needed.

Using the above expression for the energy, it is possible to recast the system of interacting electrons into a system of non-interacting electrons. The basic idea is to use the non-interacting kinetic energy as the kinetic energy term for the system, and thus to hide all other energy contributions in the potential term. To do this correctly it is necessary to examine the underlying variational problem, and

carefully designing a new potential function, the *KS-effective potential* $v_{\text{eff}}(\mathbf{r})$. This potential function is found to be (where δ denotes a functional derivative):

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \left(\frac{e_c^2}{4\pi\epsilon_0}\right) \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}), \tag{3.3}$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}, \tag{3.4}$$

where v_{xc} is the *exchange correlation potential*.

The effective potential function is designed with the primary purpose of giving the electron density of the real system from orbitals found by solving a corresponding non-interacting one particle orbital Schrödinger equation, the *KS-orbital Schrödinger equation*:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}\right)\psi_i = \epsilon_i\psi_i. \tag{3.5}$$

The orbitals obtained, ψ_i, are the *KS-orbitals*. Their corresponding energies, ϵ_i are the *KS-orbital energies*. The density of the real system is then, by construction of v_{eff}, obtained as the density of this non-interacting orbital system (accounting with a factor of two for a double degeneracy in each orbital because of the electron spin):

$$n(\mathbf{r}) = 2\sum_i^N |\psi_i(\mathbf{r})|^2. \tag{3.6}$$

The total energy of the real system is obtained by inserting this density into the total energy functional, $F[n] + V[v, n]$. The presented set of equations, Eqs. (3.3)–(3.6), are usually referred to as the *KS equations*.

However, the definition of v_{eff} includes the electron density, which is the quantity we are solving for. Thus, for a normal quantum chemistry problem where electrons are moving in a known external potential generated by the nuclei, one has to solve the KS-equations in iterative steps. Classically this is done by cyclically going through the equations, each time using the last obtained density to construct a new v_{eff}, until self consistency is attained. There also exist more refined approaches that converge faster towards the right density (and arguably more reliably).

3.2 The Kohn–Sham Orbitals

It is important to note that the KS-orbitals, ψ_i in Eq. (3.5) is not the actual electronic orbitals in the interacting multi electron system. The KS-orbital Schrödinger equation is obtained from a mathematical trick and is designed to give the correct density in Eq. (3.6), not to give the correct orbital description of the system. In the same way there is no reason to expect any simple interpretation of the KS-orbital energies, ϵ_i, in Eq. (3.5). It is, despite this, quite common

to take the KS-orbitals and energies as approximations for the real orbitals and energies and the results are usually surprisingly good.

3.3 The Exchange Correlation Energy

To be able to use the Kohn–Sham scheme above one needs an explicit expression for the exchange correlation energy, E_{xc}. It is clear that E_{xc} cannot, in any sense, be a local quantity, as it is independent of space coordinates and is equally affected by all changes throughout the system. For further analysis, and to develop useful approximations, E_{xc} is split into a sum of contributions that, arguably, will be local. This gives the *exchange correlation energy density*, ϵ_{xc} defined in every point of space, $\epsilon_{xc}([n]; \mathbf{r})$, and is assumed to show some kind of 'locality' in the sense of being mostly dependent on the part of the density which is close to $\mathbf{r}$. It is defined implicitly as giving the exchange correlation energy by integration:

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}([n]; \mathbf{r})d\mathbf{r}. \tag{3.7}$$

The implicit definition of $\epsilon_{xc}([n]; \mathbf{r})$ makes several choices possible, since the only requirement is that it should integrate to the total exchange correlation energy. This freedom of choice is important for the subsystem functional approach and will be discussed more in chapter 4. Following the formalism of Kohn and Mattsson,[4] the most common choice will be described using the *inverse radius of the exchange correlation hole*, R_{xc}^{-1}, to which $\epsilon_{xc}([n]; \mathbf{r})$ is simply related as:

$$\epsilon_{xc}^{\mathrm{irxh}}([n]; \mathbf{r}) = -\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\frac{1}{2}R_{xc}^{-1}([n]; \mathbf{r}), \tag{3.8}$$

$$R_{xc}^{-1} = -\int \frac{n_{xc}(\mathbf{r}; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}', \tag{3.9}$$

where $n_{xc}(\mathbf{r}; \mathbf{r}')$ is the conventional *exchange correlation hole density.*[*]

In this work the primary focus is on the exchange part of $\epsilon_{xc}([n]; \mathbf{r})$. The quantity n_{xc} can be split into the *exchange hole density*, n_x, and the *correlation hole density*, n_c, as follows:

$$n_{xc} = n_x + n_c, \tag{3.10}$$

$$\epsilon_{xc}^{\mathrm{irxh}} = \epsilon_x^{\mathrm{irxh}} + \epsilon_c^{\mathrm{irxh}}, \tag{3.11}$$

$$\epsilon_x^{\mathrm{irxh}}([n]; \mathbf{r}) = \left(\frac{e_c^2}{4\pi\epsilon_0}\right)\int \frac{n_x(\mathbf{r}; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}', \tag{3.12}$$

$$\epsilon_c^{\mathrm{irxh}}([n]; \mathbf{r}) = \left(\frac{e_c^2}{4\pi\epsilon_0}\right)\int \frac{n_c(\mathbf{r}; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}'. \tag{3.13}$$

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[*]It is a matter of conventions if one regards $n_{xc}(\mathbf{r}; \mathbf{r}')$ as a well defined quantity, or if one considers Eqs. (3.8) and (3.9) as definitions and regards $n_{xc}(\mathbf{r}; \mathbf{r}')$ as the source of non-uniqueness. Both viewpoints have been present in recent works of different authors. We will only use $n_{xc}(\mathbf{r}; \mathbf{r}')$ to mean the conventional, unique, definition.

Here ϵ_x is the *exchange energy per particle* and ϵ_c the *correlation energy per particle*. The exchange hole can be expressed unapproximated in the KS orbitals:

$$n_x(\mathbf{r}; \mathbf{r}') = -\frac{1}{2}\frac{|\rho_1(\mathbf{r}; \mathbf{r}')|^2}{n(\mathbf{r})},\tag{3.14}$$

$$\rho_1(\mathbf{r}; \mathbf{r}') = 2\sum_\nu \psi_\nu(\mathbf{r})\psi_\nu^*(\mathbf{r}'),\tag{3.15}$$

where $n_x(\mathbf{r}; \mathbf{r}')$ is the *exchange hole density* and $\rho_1(\mathbf{r}; \mathbf{r}')$ the *first-order spinless density matrix*.

There are two important relations involving n_x and n_c, valid for all $\mathbf{r}$:

$$\int n_x(\mathbf{r}; \mathbf{r}')d\mathbf{r}' = -1, \quad \int n_c(\mathbf{r}; \mathbf{r}')d\mathbf{r}' = 0.\tag{3.16}$$

3.4   Local Density Approximation, LDA

The first and most simple approximation of the exchange correlation energy is the *local density approximation* (LDA), proposed by Kohn and Sham[2] in their first work on DFT. LDA sets ϵ_{xc} in every space point $\mathbf{r}$, with density $n(\mathbf{r})$, equal to E_{xc} per electron of a system with a constant v_{eff} (a uniform electron gas) chosen to make the density of the uniform system equal to $n(\mathbf{r})$. It is straightforward to derive the exchange part of LDA; the KS orbitals for a constant effective potential (plane waves) are inserted into Eq. (3.8), which gives a constant ϵ_x^{irxh}, that can be parameterized in the uniform electron density to give:

$$\epsilon_x^{\text{LDA}}(n(\mathbf{r})) = -e^2\frac{3}{4\pi}\left(3\pi^2 n(\mathbf{r})\right)^{1/3}.\tag{3.17}$$

The correlation part of LDA was first estimated by Wigner[14] and more recently numerically computed by Monte Carlo calculations[15] (there are several different parameterization of the Monte Carlo data, for example the one by Perdew and Zunger[16]).

LDA was constructed as a suitable approximation for systems with very slowly varying electron densities, but it was found remarkably successful for wider use. It is still often used for electronic structure calculations of solid materials, although this is outside its formal region of validity. The accepted explanation to the success of LDA is that, apart from just being a 'sane' approximation of the real exchange-correlation energy, it also fulfills several constraints which it is known that the real exchange-correlation energy functional must fulfill.

3.5   Gradient Expansion Approximation, GEA

Even in the earliest works of DFT there was some work done towards improving the LDA by extending it through a gradient expansion approximation (GEA).

In every space point LDA just uses the local value of density. The basic idea behind the GEA is that this can be seen as using the first term in a power expansion in the local variation of the density. Hence the idea is to construct an approximation of ϵ_{xc} as a power expansion in the density and its derivatives. For a proper power expansion to second order, taking several known symmetries into account, terms proportional to two derivatives are needed. These derivatives are usually put into dimensionless quantities. The *dimensionless gradient*

$$s = \frac{|\nabla n(\mathbf{r})|}{2(3\pi^2)^{1/3} n^{4/3}(\mathbf{r})}. \tag{3.18}$$

and the *dimensionless Laplacian*

$$q = \frac{\nabla^2 n(\mathbf{r})}{4(3\pi^2)^{2/3} n^{5/3}(\mathbf{r})}. \tag{3.19}$$

However, based on the freedom of choice of the definition Eq. (3.7) it is possible to use integration by parts to eliminate the q-term. The resulting expression for the GEA is

$$\epsilon_x^{\text{GEA}}\big(n(\mathbf{r}), |\nabla n(\mathbf{r})|\big) = \epsilon_x^{\text{LDA}}\big(n(\mathbf{r})\big)\left(1 + \frac{10}{81} s^2\right), \tag{3.20}$$

In a truly slowly varying system, the GEA should perform well, but outside of its area of formal validity the GEA is found to be unsatisfactory when applied in computations. The fact that it often is less accurate than the LDA is somewhat disappointing. However, GEA has successfully been used in the derivation of modern nonempirical functionals as the limit of low-density variation, this approach has given very useful functionals (eg. certain GGAs,[17, 18] see Sec. 3.6).

There was much ado before the correct gradient coefficient, $10/81$, was established. First Sham performed[19] a calculation based on the correlation methods of Ma and Brueckner[20] and obtained a value of $7/81$. Another calculation of Gross and Dreizler[21] also gave the same result; but empirical results[22] indicated that the value was too low. Antoniewicz and Kleinman obtained $10/81$, and after some suggestion of Perdew and Wang,[23] Kleinman and Lee[24] numerically demonstrated that the cause of the confusion was an order of limits problem between the Yukawa screening factor $\bar{k}_{\text{Y}}$ and the wave vector of the density variation K. The problem is nicely exemplified by a (here slightly modified) proposed guess of a possible explicit form by Perdew and Wang:

$$\epsilon_x(K, \bar{k}_{\text{Y}}) = \frac{7}{81} + \frac{3}{81}\frac{K^2}{K^2 + \bar{k}_{\text{Y}}^2}. \tag{3.21}$$

It is found that

$$\lim_{\bar{k}_{\text{Y}} \to 0} \lim_{K \to 0} \epsilon_x(K, \bar{k}_{\text{Y}}) = 7/81 \ \ (\text{Sham result}), \tag{3.22}$$

$$\lim_{K \to 0} \lim_{\bar{k}_{\text{Y}} \to 0} \epsilon_x(K, \bar{k}_{\text{Y}}) = 10/81 \ \ (\text{Antoniewicz–Kleinman result}). \tag{3.23}$$

The plots of Kleinman and Lee[24] indicate that the qualitative behavior of this toy model is not far from the truth. Given this, it is evident that the 'right' answer is the Antoniewicz–Kleinman result, because in a true Coulomb system the Yukawa screening factor is identically zero, and hence must always be smaller than the wave vector of the density variation, that only tends to zero as we approach a slowly varying density.

However, in the successive papers of Antoniewicz, Kleinman and Lee there appear some comments regarding whether the right gradient coefficient may be dependent on how the correlation energy term is obtained, i.e., that perhaps the errors in the Sham exchange are cancelled by errors in the Ma–Brueckner correlation (since they are obtained in similar ways this is not too unlikely). Whether this issue was finally resolved or not is unknown to the author.

3.6   Generalized-Gradient Approximations, GGAs

An abstract definition of a *Generalized-Gradient Approximation* (GGA) is simply a quantity that given the local value of the density and its gradient, s^2, produces an approximation of the exchange-correlation energy per particle, i.e.:

$$E_{xc}^{\text{GGA}} = \int \epsilon_{xc}^{\text{GGA}}(n(\mathbf{r}), s^2)d\mathbf{r}. \qquad (3.24)$$

Roughly the idea is that a GGA should be constructed to produce good results for a wide range of density variations; perhaps using the GEA as a constraint for slowly varying densities, and some other known property for more rapidly varying densities. Further constraints are commonly taken from the exact conditions that the real exchange-correlation energy functional is known to fulfill (previously mentioned when explaining the success of LDA). The aim is a simple expression on closed form, which can be used for real calculations.

One usually distinguishes between empirical and non-empirical GGAs. Empirical GGAs use experimental or otherwise known results to adjust the parameters in the expression, whereas non-empirical GGAs should only use parameters derived from basic physical (quantum mechanical) principles. The common sense is that it is possible to obtain very accurate results using an empirical GGA adjusted for some precise class of systems; but that same GGA may perform poorly if applied to something that is slightly outside this class. In contrast, a good non-empirical GGA can be applied to a wide variety of problems. Because of this, to use an empirical GGA when there is no other (eg. experimental) result to compare with seems (at least to a physicist) somewhat dangerous.

Currently a large number of good GGAs are in use within quantum chemistry, materials physics and other areas. But expressions have also been developed with more complicated input parameters, such as the Laplacian q and kinetic energy densities.

3.7   The Chemical Potential

We will be referring frequently to the *chemical potential*, μ, in the following chapters. The chemical potential is a term from statistical mechanics, interpreted as the energy needed to add a particle to a multi particle system. In density functional theory it enters with the requirement that the density should integrate to the total number of particles. In an electron system at zero temperature the chemical potential is half way between the energy of the highest occupied orbital and the lowest unoccupied. It can be seen that this also holds for the KS-orbital energies, and thus the KS-orbital energies fulfill:

$$\epsilon_i \leq \mu \quad \forall \text{ occupied } i. \tag{3.25}$$

Chapter 4

Subsystem Functionals

The subsystem functional approach was mentioned in the introduction, but will now be discussed in more detail. Note however, that the paper in part II of this thesis also presents the subsystem functional approach in some detail.

4.1   General Idea

The subsystem functional approach is mostly based on the idea of locality (near-sightedness) of the electron behavior, which has previously been discussed in other works.[3,4] The general idea is that in most electron systems, the main effect on a given electron is caused by the closest of the other electrons, and thus its behavior should be governed by local or semi-local properties of the electron cloud. There are, however, some well known situations where this statement is known not to be true, eg., superconducting systems.

The starting point is the implicit definition of the exchange correlation energy per particle:

$$E_{xc} = \int n(\mathbf{r})\epsilon_{xc}(\mathbf{r})d\mathbf{r}. \tag{4.1}$$

The integration, to be taken over the whole system, may be decomposed into integrations over several separate regions:

$$E_{xc} = \int_{R_1} n(\mathbf{r})\epsilon_{xc}(\mathbf{r})d\mathbf{r} + \int_{R_2} n(\mathbf{r})\epsilon_{xc}(\mathbf{r})d\mathbf{r} + ... + \int_{R_N} n(\mathbf{r})\epsilon_{xc}(\mathbf{r})d\mathbf{r}. \tag{4.2}$$

This general idea was illustrated in chapter 1 in Fig. 1.1.

Approximations of ϵ_{xc} which can be applied in this way, i.e., using different approximations in each individual region, are referred to as *subsystem functionals*. Obviously, a subsystem functional may not be derived based on the assumption that individual integrations of Eq. (4.2) are taken over the whole system. Rather, when integrated over only a part of a system, a subsystem functional must give a valid approximation of the integrated value of some exact ϵ_{xc} in that

part. Another view of this is that, given the freedom of choice of ϵ_{xc} in Eq. (3.7) it is necessary for all subsystem functionals applied to the same system to approximate integrated values of precisely the same choice of ϵ_{xc}. This requirement is needed to ensure that the correct total exchange correlation energy results from the sum of contributions from the different parts. It is demonstrated in the paper in part II of this thesis how this requirement is enforced if all subsystem functionals applied to a system are taken to approximate one common, explicitly defined, ϵ_{xc}, such as, for example, the irxh-based definition of Eq. (3.8).

All the ideas presented here have been expressed in the coordinate space, but it is also possible to consider a partition in k-space (i.e., by performing a Fourier-transform of Eq. (4.1) before partitioning the integral). This is just briefly mentioned here, and has not been formally investigated. Such an investigation must probably begin with a careful examination of what concept of locality should be employed, giving an idea of the kind of systems where this approach can be successfully used.

4.2   Current Status of the Subsystem Functional Approach

Modern functionals in use today (eg. GGAs) have usually been derived utilizing integration by parts and other methods that assume that they are to be used throughout the whole system, and thus cannot be used in only a partial region. Because of this, for the subsystem functional scheme to be successful, it is necessary to create a GGA-like functional conforming to the subsystem functional requirements. Much of the paper in part II of the thesis is devoted to this approach; i.e., trying to unravel necessary information to create such a functional.

We have currently not discussed the non-trivial problem of performing the partitioning of a system. If a wide range of subsystem functionals was available, they could either be carefully combined by computational scientists targeting some specific system, or be composed into more general functionals applicable to a general set of problems, such as systems with electronic edges (which was the aim of the work of Kohn and Mattsson[4] referred to in the introduction in chapter 1). However, it seems fruitless to speculate in how to construct useful constraints on the partitioning before characteristics of specific subsystem functionals are known.

4.3   Related Efforts

Here the subsystem functional approach has been presented on an abstract level, but several efforts that can be seen as related have been used in actual DFT calculations. For example, Vitos *et al.* developed the *Local Airy Gas* (LAG)[25] functional. Roughly, it corresponds to using the Airy Gas exchange energy per

particle and the LDA correlation energy per particle in the edge region, while using LDA exchange and correlation energies per particle in the interior region. This functional is briefly discussed in the paper in part II of this thesis. Another example is so called hybrid functionals. They have been successfully employed in calculations, which are combining very different functionals within one system. However, usually hybrid functionals do not partition the system into regions, but rather combine a number of functionals to be used simultaneously throughout the whole system.

Chapter 5

The Mathieu Gas as a DFT Model System

Much of the scientific work in this thesis is based on the numerical study of a simple model system, the Mathieu Gas (MG). This chapter introduces the MG and discusses its usefulness as a DFT model system.

5.1 Definition of the MG

The MG can be viewed as a family of electron densities parameterized by two dimensionless scalar parameters, $\bar{\lambda}$ and $\bar{p}$. The electron densities are obtained from a noninteracting system of electrons moving in an external potential

$$v_{\text{eff}}(\mathbf{r}) = \mu\bar{\lambda}(1 - \cos(2\bar{p}k_{F,u}z)). \tag{5.1}$$

Here μ is the chemical potential and $k_{F,u}$ is the Fermi wave vector of a uniform electron gas with μ as its chemical potential. By solving the corresponding non-interacting electron system for specific $\bar{\lambda}$ and $\bar{p}$, KS orbitals, and consequently a density, are obtained.

5.2 Electron Densities of the MG Model

Solving the MG effective potential system for the KS orbitals is significantly simpler than solving a general non-interacting electron system, since the system is essentially one-dimensional. The one-dimensional nature of the system makes the KS-orbital Schrödinger equation separable, which reduce the Fermi edge to just a point (indicating where the one-dimensional integration should stop). In a real, non-separable three-dimensional system, the Fermi edge may describe a complicated curve, and may not be as easily treated.

The two constant x and y dimensions are separately handled, giving a KS orbital of the form:

$$\psi_\nu(x,y,z) = \frac{1}{\sqrt{L_1 L_2}} e^{i(k_1 x + k_2 y)}\, \varphi_\eta(z), \qquad (5.2)$$

where ν specifies k_1, k_2 and η; $L_1 L_2$ is the x, y area of the system and will approach infinity; and $k_i L_i = 2\pi m_i$ ($i = 1, 2$, m_i integer), and finally $\varphi_\eta(z)$ is the one-dimensional z-direction KS orbital. The resulting one dimensional eigenvalue equation now becomes:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + v_{\text{eff}}(z) - \epsilon_\eta\right)\varphi_\eta(z) = 0, \qquad (5.3)$$

Inserting the MG v_{eff} gives a Mathieu differential equation with known solutions (see Ref. 26 for definitions of the Mathieu function symbols, se_η, ce_η, a_η and b_η)

$$\varphi_\eta(z) = \begin{cases} (1/\sqrt{L})\, ce_\eta(pk_{F,u}z, -\bar{\lambda}/\bar{p}^2) & \text{if } \eta > 0 \\ (1/\sqrt{L})\, se_\eta(pk_{F,u}z, -\bar{\lambda}/\bar{p}^2) & \text{if } \eta < 0 \end{cases} \qquad (5.4)$$

$$\epsilon_\eta = \begin{cases} \bar{p}^2 a_\eta + \bar{\lambda} & \text{if } \eta > 0 \\ \bar{p}^2 b_\eta + \bar{\lambda} & \text{if } \eta < 0 \end{cases} \qquad (5.5)$$

$$n(\mathbf{r}) = \frac{k_{F,u}^3}{4\pi^2}\bar{p} \int_{-\tilde{\eta}}^{\tilde{\eta}} L|\varphi_\eta(z)|^2 \left(1 - \frac{\epsilon_\eta}{\mu}\right) d\eta, \qquad (5.6)$$

where $\tilde{\eta}$ should be the largest possible η that fulfills $\epsilon_\eta \leq \mu$.

However, we are still left with the issue of finding suitable numerical routines for calculating the values of the Mathieu functions ce and se. In fact, the method of obtaining explicit numerical values for the Mathieu functions is to go back to the differential equation, Eq. (5.3), and solve it by standard matrix methods; very much like a generalized DFT-program would. This method is presented in some detail in the paper in part II of the thesis. Furthermore, when the KS orbitals are known they can also be inserted into the equations for the exchange part of the exchange-correlation energy per particle, Eq. (3.12), (3.14) and (3.15). This is essentially how the data was obtained for the plots in Figs. 7–12 of the paper in part II.

From a careful analysis of the energy expression, Eq. (5.5), it is seen that the MG shows a rudimentary energy-band structure. The index η acts as a dimensionless scaled wave-vector, that indexes this band structure, very much like the wave vector in an extended Brillouin zone-scheme.

5.3   Exploring the Parameter Space of the MG

The MG model spans a wide variety of systems over the range of possible $\bar{\lambda}$ and $\bar{p}$. Apart from the limit of slowly varying densities, which naturally has been of interest in the pursuit of a functional working for such densities, we have also found it very useful to investigate some specific limits in the MG as they are model systems in their own right.

5.3.1 The Limit of Slowly Varying Densities

From the construction of the MG family of densities it follows that the limit of slowly varying densities is found as $\bar{\lambda}$, $\bar{p} \to 0$. However, the two-dimensionality of this limit makes it challenging to analyze the evaluated numerical data in a consistent way. This is one of the larger issues with the data analysis of DFT quantities in the MG gas. In the present work this was handled by plotting calculated data versus a combination of the two parameters, that essentially equalized similar behavior of the curves. The creation of such a parameter is based on the observation that the shape of the curves of most DFT quantities are closely related to the energy structure of the non-interacting electron system used to construct the MG family of densities. A suitable choice of such an energy related parameter was constructed as:

$$\alpha = \frac{\mu - \epsilon_{\eta_1}}{\epsilon_{\eta_2} - \epsilon_{\eta_1}} + |\eta_1|, \tag{5.7}$$

where, if μ is inside a z-dimension energy band, ϵ_{η_1} is the lowest energy in this band. If μ is not inside an energy band, ϵ_{η_1} is the lowest energy in the band which contains the z-dimension energy state with highest energy $\leq \mu$. Furthermore, ϵ_{η_2} is the lowest possible energy of all z-dimension energy states within bands that only contain energies $> \mu$. By construction η_1 and η_2 are integer.

The parameter α describes the position of the chemical potential relative to the lower band edges, that is, the lowest energies of the energy bands in the z dimensional energy band structure. The parameter α differs from η in that it indexes values of the chemical potential both within and between the energy bands in the z dimension, making it useful throughout the parameter space of the MG.

5.3.2 The Free Electron Gas Limit

When $\bar{\lambda} \to 0$, the MG effective potential, Eq. (5.1), approaches a constant potential. This makes the solutions to the MG differential equation approach plane wave solutions to a free electron (FE) gas:

$$\varphi_\eta(z) = \frac{1}{\sqrt{L_3}} \exp(i\eta\bar{p}\bar{z}), \tag{5.8}$$

$$\epsilon_\eta = \mu\eta^2\bar{p}^2. \tag{5.9}$$

Hence, in this limit the MG densities show similarities to a system with an infinite, weakly perturbed, system. Disregarding the one-dimensionality of the MG effective potential, by moving away from the FE limit in the right direction, the MG should, in a very abstract sense, appear much like an infinite, slowly varying, crystal.

We also note that specifically in the FE limit, the α parameter can be simplified to

$$\alpha_{FE} = \frac{1/\bar{p}^2 + N(N+1)}{2N+1}, \quad N = \left\lfloor \frac{1}{\bar{p}} \right\rfloor. \tag{5.10}$$

5.3.3   The Harmonic Oscillator Limit

We will now study the limit $\bar{\lambda}/\bar{p}^2 \to \infty$. The MG effective potential approach an harmonic oscillator (HO), but this might not be as obvious as was the case for the FE limit. The situation might be more clear through an analysis of the energy structure, which in this limit becomes:

$$\epsilon_n = \mu\sqrt{2\bar{\lambda}\bar{p}^2}\,(2n+1). \tag{5.11}$$

This clearly describes equally spaced energy levels, with a distance of $\mu\sqrt{2\bar{\lambda}\bar{p}^2}$, which is similar to a text book HO system.

The corresponding KS orbitals are:

$$\varphi_n(z) = \left(\frac{k_{F,u}(\sqrt{2\bar{\lambda}\bar{p}^2})^{1/2}}{\sqrt{\pi}2^n n!} \right)^{1/2} H_n((\sqrt{2\bar{\lambda}\bar{p}^2})^{1/2}\bar{z})$$
$$\times \exp\left(-[(\sqrt{2\bar{\lambda}\bar{p}^2})^{1/2}\bar{z}]^2/2\right), \tag{5.12}$$

where $H_n(x)$ are Hermite polynomials[26] and $n = 0,\ 1,\ 2,\ldots$.

Finally, in the HO limit the α parameter can be simplified to:

$$\alpha_{HO} = \frac{1}{2\sqrt{2\bar{\lambda}\bar{p}^2}} - \frac{1}{2}. \tag{5.13}$$

The HO limit has turned out to be very useful in the work presented in this thesis, since it is possible to do computations for this system, i.e., as a model system in its own right instead of employing a limiting procedure in the MG. Comparing MG data in the HO limit and data for the pure HO gives an extra check on the numerics. Also, in a very abstract sense, the HO limit can be said to mimic an atomic-like system, as it effectively is of finite size in the z dimension. Hence, this limit and the 'crystal like' FE limit previously mentioned are fundamentally different.

Chapter 6

Investigation of the Kinetic Energy Density

This chapter investigates the power expansion of the kinetic energy density. Although this power expansion is already well known, the procedure provides an independent evaluation of our numerical methods. The study also serves as a simplified example of the methods of the investigation of the exchange energy per particle presented in the paper in part II of the thesis.

6.1 Definition of the Kinetic Energy Density

The kinetic energy density $\tau(\mathbf{r})$ is a localized version of the total kinetic energy (KE) of the non-interacting KS electron system. It is designed with the same approach that led to the exchange-correlation energy per particle, Eq. (3.7). An implicit definition, much in the same style as Eq. (3.7), is (T_s was introduced in Eq. (3.1))

$$T_s[n] = \int \tau(\mathbf{r}) d\mathbf{r}. \tag{6.1}$$

The conventional definition of $\tau(\mathbf{r})$ for a spin unpolarized system is

$$\tau(\mathbf{r}) = \sum_\nu |\nabla \psi_\nu(\mathbf{r})|^2, \tag{6.2}$$

where the sum is taken over all occupied orbitals. It is known[27–29] that the second order gradient expansion of this quantity is

$$\tau_{\mathrm{exp}}(\mathbf{r}) = \tau_{\mathrm{LDA}} \left(1 + \frac{5}{27}s^2 + \frac{20}{9}q \right), \tag{6.3}$$

$$\tau_{\mathrm{LDA}}(\mathbf{r}) = \frac{3}{10}(3\pi^2)^{2/3} n(\mathbf{r})^{5/3}. \tag{6.4}$$

6.2   The KE Density in the MG

The KS orbitals corresponding to the MG family of densities can be inserted into Eq. (6.2) to compute numerical values of the kinetic energy density. It is expected that the computed values in the limit of slowly varying densities should behave accordingly to Eq. (6.3). This is investigated here by evaluating curves for a fixed $\bar{\lambda}/\bar{p}^2 = 0.8$ and plot them versus $1/\alpha$ in the limit $1/\alpha \to 0$; i.e., the limit of slowly varying densities.

Given Eq. (6.3), the following limits are expected for the MG:

$$\text{For } s^2 = 0, \ \ 1/\alpha \to 0: \quad \left(\frac{\tau(\mathbf{r})}{\tau_{\text{LDA}}} - 1 \right) /q \to \frac{20}{9}, \tag{6.5}$$

$$\text{For } q = 0, \ \ 1/\alpha \to 0: \quad \left(\frac{\tau(\mathbf{r})}{\tau_{\text{LDA}}} - 1 \right) /s^2 \to \frac{5}{27}. \tag{6.6}$$

It is simple to find a path where $s^2 = 0$ as this is always fulfilled at the minimum point of the effective potential, i.e., $z = 0$, because of symmetries. To find a path where $q = 0$, a search is implemented in the program that finds a z where this is fulfilled for every α-point to be evaluated.

6.3   Analyzing the KE Density

Plotting evaluated data for the two limits discussed above gives Figs. 6.1 and 6.2. We first note that the limiting behaviors predicted in Eqs. (6.5) and (6.6) are correctly obtained in the $1/\alpha \to 0$ limits. Apart from this expected result, it is interesting to comment on the behavior at higher $1/\alpha$. In the paper in part II of the thesis a careful study of the behavior of the electron density, the density Laplacian and the exchange energy per particle is performed. These quantities were observed to be strongly influenced by the energy structure of the MG, most clearly seen at values of α where the chemical potential is placed between energy bands[*]. We observe that the KE density also is affected by the energy structure, as the same values of α describes locations of rapid change ($1/\alpha = 1/2$ and $1/\alpha = 1/3$ in Fig. 6.1; the curve in Fig. 6.2 also changes rapidly at the first point, but it has only a small 'bump' at the second point). However, note that the variation of the KE density is on a very small scale. Plotting for yet higher values of $1/\alpha$ should give a more relevant picture of the behavior of the KE density outside the domain of slowly varying densities.

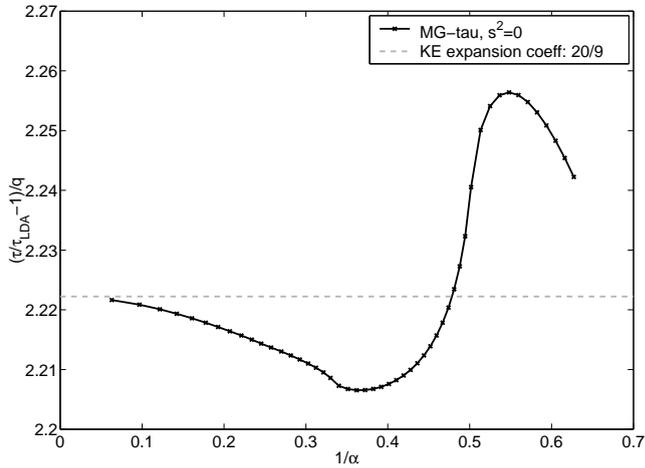[*]Refer to the paper for more details on the MG energy structure.

Figure 6.1. The quantity $(\tau(\mathbf{r})/\tau_{\mathrm{LDA}} - 1)/q$ vs $1/\alpha$ for $\bar{\lambda}/\bar{p}^2 = 0.8$ and $s^2 = 0$. In the limit of slowly varying densities, $1/\alpha \to 0$, this quantity approaches the Laplacian coefficient in the kinetic energy density power expansion, Eq. (6.3), as is expected.
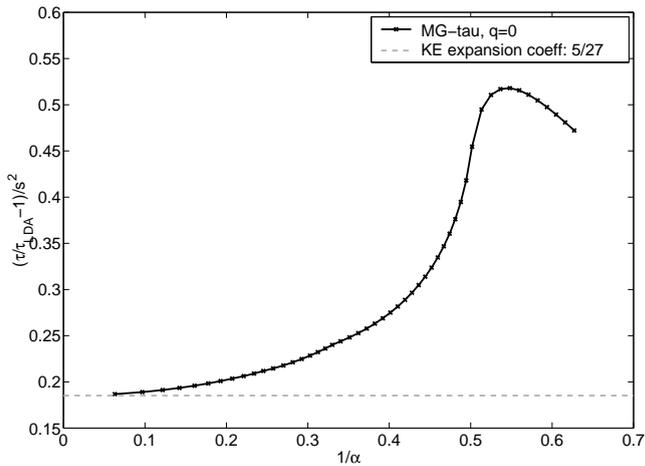

Figure 6.2. The quantity $(\tau(\mathbf{r})/\tau_{\mathrm{LDA}} - 1)/s^2$ vs $1/\alpha$ for $\bar{\lambda}/\bar{p}^2 = 0.8$ and $q = 0$. In the limit of slowly varying densities, $1/\alpha \to 0$, this quantity approaches the gradient coefficient in the kinetic energy density power expansion, Eq. (6.3), as is expected.

Chapter 7

Concluding Remarks and Comments on the Paper

The paper in part II of this thesis both presents the subsystem functional approach and examines properties of a suggested form of a subsystem functional for subsystems with slowly varying electron densities. The paper goes into details of the Mathieu Gas to make a careful data analysis possible. The exchange energy per particle is calculated and presented, giving a consistent picture of the behavior of the DFT quantities of the MG system. However, when investigating the exchange energy per particle in this system it is shown that it cannot be modeled by an ordinary power expansion. This introduces an obstacle for the subsystem functional approach, since it prevents a simple starting point for building further GGA-like functionals.

As mentioned in the conclusions of the paper, several options for future directions are possible. From work done after the paper was published, it seems that the most fruitful of these options are the parameterization of the non-analytical behavior and the approach that splits the exchange–correlation energy in some alternative way to what is traditional. We are currently working in these directions.

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Bibliography

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1964).

[3] W. Kohn, Phys. Rev. Lett **76**, 3168 (1996).

[4] W. Kohn and A. E. Mattsson, Phys. Rev. Lett. **81**, 3487 (1998).

[5] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[6] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).

[7] M. Born and J. R. Oppenheimer, Ann. Phys. **87**, 457 (1927).

[8] L. H. Thomas, Proc. Camb. Philos. Soc. **23**, 542 (1927).

[9] E. Fermi, Rend. Acad. Naz. Lincei **6**, 602 (1927).

[10] M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979).

[11] M. Levy, Phys. Rev. A **26**, 1200 (1982).

[12] M. Levy and J. P. Perdew, in *Physics as Natural Philosophy*, edited by M. F. A. Shimony (MIT, Cambridge, 1982), pp. 111–149.

[13] M. Levy and J. P. Perdew, in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum Press, New York, 1985), pp. 11–30.

[14] E. P. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[15] D. M. Ceperly and B. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[16] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1980).

[17] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[18] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. **46**, 6671 (1992).

[19] L. J. Sham, in *Computational Methods in Band Structure*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum Press, New York, 1971), p. 458.

[20] S. K. Ma and K. A. Brueckner, Phys. Rev. **165**, 18 (1968).

[21] E. K. U. Gross and R. M. Dreizler, Z. Phys. A **302**, 103 (1981).

[22] F. Herman, J. P. VanDyke, and I. B. Ortenburger, Phys. Rev. Lett **22**, 807 (1969).

[23] J. P. Perdew and Y. Wang, in *Mathematics Applied to Science*, edited by J. A. Goldstein, S. I. Rosencrans, and G. A. Sod (Academic Press, Boston, 1988), pp. 187–209.

[24] L. Kleinman and S. Lee, Phys. Rev. B **37**, 4634 (1988).

[25] L. Vitos, B. Johansson, J. Kollár, and H. Skriver, Phys. Rev. B **62**, 10 046 (2000).

[26] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1964).

[27] A. S. Kompaneets and E. S. Pavlovskii, Sov. Phys. JETP **4**, 328 (1957).

[28] D. A. Kirzhnits, Sov. Phys. JETP **5**, 64 (1957).

[29] M. Brack, B. K. Jennings, and Y. H. Chu, Phys. Lett. **65B**, 1 (1976).

Part II

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