**KTH Engineering Sciences**

# THE MANY-ELECTRON ENERGY IN DENSITY FUNCTIONAL THEORY

## From Exchange-Correlation Functional Design to Applied Electronic Structure Calculations

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## Abstract

The prediction of properties of materials and chemical systems is a key component in theoretical and technical advances throughout physics, chemistry, and biology. The properties of a matter system are closely related to the configuration of its electrons. Computer programs based on density functional theory (DFT) can calculate the configuration of the electrons very accurately. In DFT all the electronic energy present in quantum mechanics is handled exactly, except for one minor part, the exchange-correlation (XC) energy. The thesis discusses existing approximations of the XC energy and presents a new method for designing XC functionals—the subsystem functional scheme. Numerous theoretical results related to functional development in general are presented. An XC functional is created entirely without the use of empirical data (i.e., from so called first-principles). The functional has been applied to calculations of lattice constants, bulk moduli, and vacancy formation energies of aluminum, platinum, and silicon. The work is expected to be generally applicable within the field of computational density functional theory.

## Sammanfattning

Att förutsäga egenskaper hos material och kemiska system är en viktig komponent för teoretisk och teknisk utveckling i fysik, kemi och biologi. Ett systems egenskaper styrs till stor del av dess elektrontillstånd. Datorprogram som baseras på täthetsfunktionalsteori kan beskriva elektronkonfigurationer mycket noggrant. Täthetsfunktionalsteorin hanterar all kvantmekanisk energi exakt, förutom ett mindre bidrag, utbytes-korrelationsenergin. Avhandlingen diskuterar existerande approximationer av utbytes-korrelationsenergin och presenterar en ny metod för konstruktion av funktionaler som hanterar detta bidrag—delsystems-funktionalmetoden. Flera teoretiska resultat relaterade till funktionalutveckling ges. En utbytes-korrelations-funktional har konstruerats helt utan empiriska antaganden (dvs, från första-princip). Funktionalen har använts för att beräkna gitterkonstant, bulkmodul och vakansenergi för aluminium, platina och kisel. Arbetet förväntas vara generellt tillämpbart inom området för täthetsfunktionalsteoriberäkningar.

# PREFACE

This thesis presents research performed at the group of Theory of Materials, Department of Physics at the Royal Institute of Technology in Stockholm during the period 2000–2005. The thesis is divided into three parts. The first one gives the background of the research field. The second part discusses the main scientific results of the thesis. The third part consists of the publications I have coauthored. The papers provide specific details on the scientific work. Comments on these papers and details on my contributions are given in chapter 10.

## List of Included Publications

1. *Subsystem functionals: Investigating the exchange energy per particle*, R. Armiento and A. E. Mattsson, Phys. Rev. B **66**, 165117 (2002).

2. *How to Tell an Atom From an Electron Gas: A Semi-Local Index of Density Inhomogeneity*, J. P. Perdew, J. Tao, and R. Armiento, Acta Physica et Chimica Debrecina **36**, 25 (2003).

3. *Alternative separation of exchange and correlation in density-functional theory*, R. Armiento and A. E. Mattsson, Phys. Rev. B **68**, 245120 (2003).

4. *A functional designed to include surface effects in self-consistent density functional theory*, R. Armiento and A. E. Mattsson, Phys. Rev. B **72**, 085108 (2005).

5. *PBE and PW91 are not the same*, A. E. Mattsson, R. Armiento, P. A. Schultz, and T. R. Mattsson, to be submitted for publication.

6. *Numerical Integration of functions originating from quantum mechanics*, R. Armiento, Technical report (2003).

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*If we wish to understand the nature of reality, we have an inner hidden advantage: we are ourselves a little portion of the universe and so carry the answer within us.*

Jacques Boivin

Part I

# Background

## Chapter 1

# INTRODUCTION

> *The whole is greater than the sum of its parts.*
> *The part is greater than its role in the whole.*
>
> Tom Atlee

The interplay of theoretical and experimental physics during the last century has led to a successful model for the composition and interaction of matter on a very small scale. In 1897 Thomson discovered the negatively charged *electron*. The experiments of Rutherford and coworkers in 1909 lead to the conclusion that matter consists of separated positively charged *nuclei*. Following this, in 1913 Bohr created a successful model for the building blocks of matter as composed by nuclei orbited by electrons subject to certain rules. During the 1920s Heisenberg and Schrödinger were two key players in the construction of a mathematical framework that provides a precise mathematical description of the behavior of the particles, *quantum mechanics*. The scientific progress following the work of these pioneers and others has resulted in a conceptual view of matter as composed of *subatomic particles*, which interact according to the laws of quantum mechanics to form *atoms* (cf. Fig. 1.1).

It is often observed how the combination of a large number of small parts gives a resulting compound system that shows properties not evident from the properties of the individual parts. This is known as the phenomenon of *emergent properties*. In the present context, even though we have detailed knowledge from quantum mechanics about the physics governing electrons and nuclei, a piece of solid material has properties that are very much non-obvious and sometimes even outright surprising (e.g., high temperature superconductivity).

Modern computers provide a seemingly straightforward approach to handle emergent properties. A *brute force* computational physics approach would be to simulate a system in a computer program by using the detailed quantum mechanical mathematical description of a large number of nuclei, electrons, and their interactions. However, even for a few dozen atoms this approach results in a computer program which will take much too long

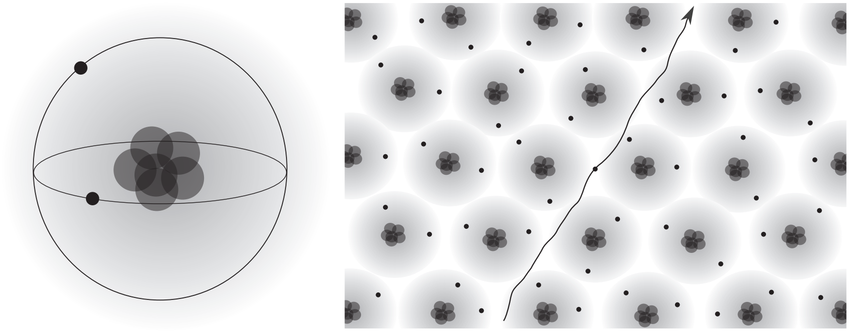

**Figure 1.1.** (left) A conceptual sketch of the atomic model: a positively charged nucleus is surrounded by an electronic cloud built up from individual electrons. (right) A conceptual sketch of a few atoms in a crystalline solid. The solid curve illustrates the idea that some individual electrons may be weakly bound and travel through the material. These are only conceptual sketches, and not to scale. Real electronic orbitals are usually more complicated than illustrated here.

time to run even for an extremely powerful computer. One can even question whether such a brute force computational approach is a scientifically legitimate concept. A reasonable simulation of a system with as few as 1000 electrons would require the computer's memory to keep track of more information bits than the number of particles in the universe. The exponential growth of the required memory with the number of electrons has been referred to as the Van Vleck catastrophe[1]. Note that a calculation for a full simulation of just a few grams of carbon would involve more than $10^{23}$ electrons. Hence, it is misguided to claim that the knowledge of the basic laws of quantum mechanics makes all emergent properties of matter understood.

It is thus obvious that refined mathematical models are needed for all but the most trivial computational studies of material properties. One such refinement is the density functional theory (DFT)[2,3]. In DFT the quantum mechanical theory is reformulated to model the electrons as a compound cloud, an *electron gas*. The reformulation focuses on the density of electrons, rather than on individual electrons (cf. Fig. 1.2). The benefit of the electron gas view is that no matter how many electrons are involved, the density of electrons remains a three-dimensional quantity (a 'field'). In contrast, to keep track of all individual electrons, a quantity of a dimensionality proportional to the number of electrons is needed. The price paid for the simpler description of DFT is that one loses the ability to describe the properties of the system that are related to the motion of individual electrons. For other properties, the DFT picture is as theoretically fundamental as the view of individual interacting electrons[1,2].

*Energy* is a fundamental property in physics. Physical mechanisms induce 'changes' in a system's state, and all such changes involve some kind of energy transfer. Hence, a way to describe the system's energy as a function of its state is also a description of the underlying physical mechanisms. Such an energy function shows what changes the system is likely to

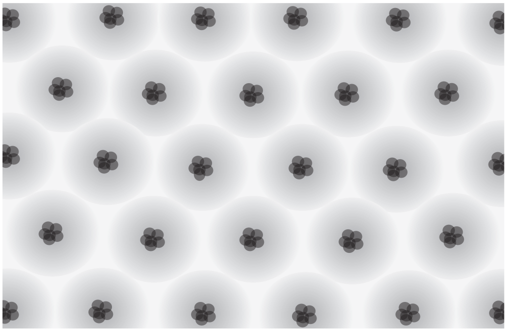

**Figure 1.2.** A conceptual sketch of the DFT view of a crystalline solid; there are no individual electrons, but only a three-dimensional density of electrons.

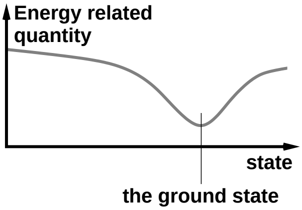

**Figure 1.3.** A schematic sketch of how the ground state of a system is found as a stable minimum of an energy related quantity. What specific energy related quantity is used depends on what environment the system is placed in.

undergo, and what state the system naturally prefers in an external environment; i.e., its *ground state*. The ground state is the state where no change is induced, which means that it is a *stable minimum* of an energy-related quantity (see Fig. 1.3). The accurate computation of the energy of a matter system therefore is of much interest, and is the focus of this thesis.

The DFT reformulation of quantum mechanics can be transformed into a form suitable for computer calculations of a system's energy[3]. The most difficult quantum mechanical behavior of the interaction of electrons is put into a quantity called the *exchange-correlation energy functional*, $E_{xc}$. This quantity is usually of minor magnitude, but except for some fundamental assumptions, it turns out to be the only part that has to be approximated relative to a brute force quantum mechanical solution. Thus, all that is 'lost' in a DFT calculation is condensed into the exchange-correlation energy functional. Hence, increasingly accurate approximations to $E_{xc}$ provide a better and better description of matter.

The scientific contribution of this thesis is focused on the development and testing of an approach for the construction of more accurate exchange-correlation functionals. The main underlying idea is that a system can be split into several regions. In each region

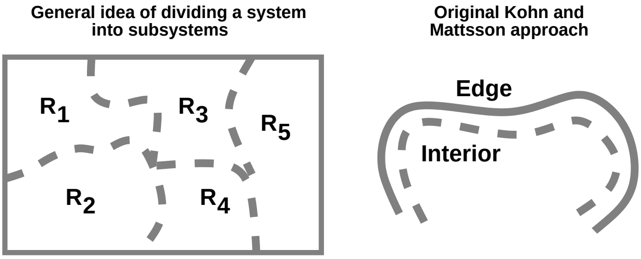
General idea of dividing a system into subsystems
R1
R3
R5
R2
R4
Original Kohn and Mattsson approach
Edge
Interior

**Figure 1.4.** An illustration of the idea that a system can be divided into subsystems, where different functionals are used in the different regions $R_1$, $R_2$, ....

a different approximation of $E_{xc}$ can be used. Each such approximation can then be specifically designed for the part of the system it is applied to. This idea is based on the locality, or 'near-sightedness', of a system of electrons[4,5]. Kohn and Mattsson have suggested the possibility to split a system into specific interior and edge parts[5]. The here discussed generalized approach is illustrated in Fig. 1.4.

The main scientific contributions presented in this thesis can be summarized as:

- The theoretical development of a scheme for functional development in density functional theory based on the partitioning of the electron density into regions with different properties—the subsystem functional scheme.
- The creation of a simple first-principles exchange-correlation energy functional, using the subsystem functional approach. The functional uses a targeted treatment for electron density 'surfaces'.
- Discussion and development of density indices as a means for automatic classification of regions of an electron density.
- The development and study of an advanced DFT model system, the Mathieu gas.
- The construction of a 'local' gradient expansion approximation.

## 1.1 Units and Physical Constants

This thesis uses SI units. See Appendix A for more information on unit systems. The following physical constants are used:

| | | |
|---|---|---|
| Electron charge | $e_c$ | $\approx 1.6022 \cdot 10^{-19}$ C |
| Electron mass | $m_e$ | $\approx 9.1094 \cdot 10^{-31}$ kg |
| Planck's constant | $\hbar$ | $\approx 1.0546 \cdot 10^{-34}$ J s |
| Permittivity of free space | $\epsilon_0$ | $\approx 8.8542 \cdot 10^{-12}\ \mathrm{C^2/(N\,m)}$ |
| Bohr radius | $a_0$ | $= 4\pi\epsilon_0\hbar^2/(m_e e_c^2) \approx 5.2918 \cdot 10^{-11}$ m |
| Speed of light | $c$ | $= 2.99792458 \cdot 10^8$ m/s |

## Chapter 2

# DENSITY FUNCTIONAL THEORY

*I am your density! I mean, your destiny.*

George McFly in the movie 'Back to the Future'

This chapter introduces the theoretical framework of density functional theory (DFT). We start from the Schrödinger equation and rewrite the problem of electron interactions into its DFT equivalent. In the end, the ground state electronic energy of a system of interacting electrons is shown to be given by a minimization over electron densities of a total electronic energy functional. There are many textbooks and other sources treating DFT, for example Refs 6–9.

## 2.1 The Many-Electron Schrödinger Equation

Our starting point is the *time independent non-relativistic Schrödinger equation* that describes a system of matter. It is the eigenvalue equation for the total energy operator, the *Hamiltonian* $\hat{\mathrm{H}}$. The equation defines all *states* $\Psi$ of the system and their related energies $E$:

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

In the usual model of matter, with electrons in the presence of the positively-charged nuclei, it is common to assume that the Schrödinger equation can be separated into independent electronic and nucleonic parts. This is the *Born-Oppenheimer approximation*[10], which is valid when the electrons reach equilibrium on a time scale that is short compared to the time scale on which the nuclei move. The approximation separates the states into independent states for nuclei $\Psi_n$ and electrons $\Psi_e$, with energies $E_n$ and $E_e$. The Hamiltonian is split into corresponding terms, $\hat{\mathrm{H}}_n$ and $\hat{\mathrm{H}}_e$. The interaction energy between nuclei and electrons is placed in the electronic part. The result is

$$\Psi = \Psi_n \Psi_e, \quad \hat{\mathrm{H}} = \hat{\mathrm{H}}_n + \hat{\mathrm{H}}_e, \tag{2.2}$$

$$\hat{\mathrm{H}}_n \Psi_n = E_n \Psi_n, \tag{2.3}$$

$$\hat{\mathrm{H}}_e \Psi_e = E_e \Psi_e. \tag{2.4}$$

The nucleonic part is uncomplicated to handle. Our concern in the following therefore is the electronic part, which describes interacting electrons that moves in a static external potential created by the charged nuclei.

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

$$\hat{\mathrm{H}}_e = \hat{\mathrm{T}} + \hat{\mathrm{U}} + \hat{\mathrm{V}} = \hat{\mathrm{F}} + \hat{\mathrm{V}}. \tag{2.5}$$

Let the *spatial location* of electron $i$ be denoted $\mathbf{r}_i$; its *spin coordinate* $\sigma_i = \uparrow$ or $\downarrow$; the total number of electrons in the system $N$; and the static *external potential*, which originates from the nuclei, $v(\mathbf{r})$. We combine position and spin coordinates in one quantity $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$. In a wave-function based approach the system's electronic states are described as *many-electron wave-functions* $\Psi_e = \Psi_e(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$, subject to two conditions; they must be *normalized*

$$\langle \Psi_e | \Psi_e \rangle = \iint ... \int |\Psi_e|^2 \, d\mathbf{x}_1 d\mathbf{x}_2 ... d\mathbf{x}_N = 1, \tag{2.6}$$

and *antisymmetric*

$$\Psi_e(..., \mathbf{x}_i, ..., \mathbf{x}_j, ...) = -\Psi_e(..., \mathbf{x}_j, ..., \mathbf{x}_i, ...). \tag{2.7}$$

The state $\Psi_e$ we are interested in is the *ground state wave-function* $\Psi_0$ of energy $E_0$. It is the solution to the electronic part of the Schrödinger equation Eq. (2.4) that has the lowest energy.

The contributions to the Hamiltonian can be explicitly expressed as

$$\hat{\mathrm{T}} = -\left(\frac{\hbar^2}{2m_e}\right) \sum_{i=1}^{N} \nabla_i^2, \tag{2.8}$$

$$\hat{\mathrm{U}} = \left(\frac{e_c^2}{4\pi\epsilon_0}\right) \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{2.9}$$

$$\hat{\mathrm{V}} = \sum_{i=1}^{N} v(\mathbf{r}_i). \tag{2.10}$$

The electronic energy $E_e$ can be obtained as the *expectation value* of the Hamiltonian,

$$E_e = \langle \Psi_e | \hat{\mathrm{H}}_e | \Psi_e \rangle = \langle \Psi_e | \hat{\mathrm{T}} + \hat{\mathrm{U}} + \hat{\mathrm{V}} | \Psi_e \rangle = T + U + V =$$

$$\iint \dots \int \left( - \left( \frac{\hbar^2}{2m_e} \right) \sum_{i=1}^{N} \Psi_e^* \nabla_i^2 \Psi_e + \left( \frac{e_c^2}{4\pi\epsilon_0} \right) \sum_{i<j}^{N} \frac{|\Psi_e|^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \right.$$

$$\left. + \sum_{i=1}^{N} |\Psi_e|^2 v(\mathbf{r}_i) \right) d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N. \tag{2.11}$$

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

The *Rayleigh–Ritz variational principle*[11,12] offers a way to solve the electron energy problem to obtain the ground state wave-function $\Psi_0$ and energy $E_0$. The ground state electronic energy is found through a search for the many-electron wave-function that minimizes the energy expectation value in Eq. (2.11),

$$E_0 = \min_{\Psi} \langle \Psi | \hat{\mathrm{H}}_e | \Psi \rangle, \quad \text{has minimum for } \Psi = \Psi_0, \tag{2.12}$$

where the search is constrained by the normalization and anti-symmetric conditions of Eqs. (2.6) and (2.7). A direct application of the Rayleigh–Ritz variational method involves a search for the minimizing wave-function in the space of functions of a dimensionality proportional to the number of electrons in the system. In the following we will instead take the DFT approach and rewrite the problem to involve a search over only three-dimensional functions, i.e., electron densities.

## 2.2 The Electron Density

The *electron density* $n(\mathbf{r})$ is defined as the number of electrons per volume at the point $\mathbf{r}$ in space. It is a physical quantity—it can (at least in theory) be measured. The integral of the electron density gives the total number of electrons,

$$\int n(\mathbf{r}) d\mathbf{r} = N. \tag{2.13}$$

The relation between $n(\mathbf{r})$ and the many-electron wave-function $\Psi_e$ is

$$n(\mathbf{r}) = N \iint \dots \int |\Psi_e(\mathbf{r}\sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 \, d\sigma_1 d\mathbf{x}_2 \dots d\mathbf{x}_N. \tag{2.14}$$

The expression on the right hand side looks similar to the wave-function normalization integration Eq. (2.6) but without one of the spatial integrals, and thus one coordinate is left free. Here we have arbitrarily removed the integration over the first coordinate $\mathbf{r}_1$, but it can be replaced by any of the spatial integrals, due to the antisymmetric property of the wave-function Eq. (2.7). The requirement that the wave-functions are normalized Eq. (2.6) guarantees that the integral of the electron density is $N$ as in Eq. (2.13).

If one looks at the three terms in the expression for the electronic energy Eq. (2.11), one sees that the term for the external potential $V$ is easily rewritten in terms of the density,

$$\begin{aligned} V &= \iint \ldots \int \sum_{i=1}^{N} |\Psi_e|^2 \, v(\mathbf{r}_i) \, d\mathbf{x}_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N = \\ &= \frac{1}{N} \sum_{i=1}^{N} \int n(\mathbf{r}_i) v(\mathbf{r}_i) d\mathbf{r}_i = \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}. \end{aligned} \tag{2.15}$$

The other two terms of the electronic energy Eq. (2.11) are not as easy to rewrite. In the kinetic energy term $T$, the derivative operator between the wave-functions prevents rewriting the integrand on the form $|\Psi_e|^2$ as needed to turn the term into an expression of the electron density. In the term of the internal potential energy $U$, the particle positions in the denominator preclude a direct term by term integration.

A *functional* is an object that acts on a function to produce a scalar. From the way the potential energy term $V$ was rewritten in Eq. (2.15), it is an explicit *potential energy functional* $V[n]$ of the electron density. This and other functionals with the electron density $n(\mathbf{r})$ as arguments are called *density functionals*. The other terms in the electronic energy Eq. (2.11) are not on explicit density functional form, but can at least be written as functionals of the many-electron wave-function $\Psi_e$,

$$E_e = T[\Psi_e] + U[\Psi_e] + V[v, n] = F[\Psi_e] + V[v, n]. \tag{2.16}$$

At this point a question central to DFT enters: *is it possible to also rewrite the total internal electronic energy $F[\Psi_e]$ as a density functional $F[n]$?* If such a functional exists, it is a *universal functional* in that it is independent of the external potential. *The same $F[n]$ may be used in any electronic energy problem.* The question of the existence of an $F[n]$ functional will be considered in the following.

## 2.3 The Thomas–Fermi Model

A rather direct approach to answer the question if there exists some, at least approximative, density functional for the total internal electronic energy $F[n]$ is to see if it can be constructed from basic physics ideas. Early attempts to create such an approximation were made by Thomas and Fermi[13–16]. They used some assumptions about the distribution and the interaction between electrons to approximate the kinetic energy. The electron density in each space point is set equal to a number of electrons in a fixed volume, $n(\mathbf{r}) = \Delta N / \Delta V$. A system of $\Delta N$ free non-interacting electrons in an infinite-well model of volume $\Delta V$ then gives an expression for the kinetic energy per volume. The continuity limit is then taken, $\Delta V \to 0$. The result is integrated over the whole space to give the approximate *Thomas–Fermi functional* for the total kinetic energy $T_{TF}[n]$,

$$T \approx T_{TF}[n] = \frac{3}{5}(3\pi^2)^{2/3}\left(\frac{\hbar^2}{2m_e}\right)\int n^{5/3}(\mathbf{r})d\mathbf{r}. \tag{2.17}$$

Furthermore, the *electrostatic energy of a classical repulsive gas* $J[n]$ can be used as a simplistic approximation of the internal potential energy $U$,

$$U \approx J[n] = \frac{1}{2}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\iint \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2. \tag{2.18}$$

The result is the *Thomas–Fermi model*:

$$E_e \approx T_{TF}[n] + J[n] + \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \tag{2.19}$$

The Thomas–Fermi approximation to the internal electronic energy thus is

$$F[n] \approx T_{TF}[n] + J[n]. \tag{2.20}$$

## 2.4 The First Hohenberg–Kohn Theorem

The early efforts to find and use internal electronic energy functionals $F[n]$ by Thomas and Fermi, and extensions along the same ideas, were all based on 'reasonable' approximations. It is a great conceptual difference between such rather heuristic approaches and the more rigorous theoretical framework that followed the work of Hohenberg and Kohn[2]. Two famous theorems proved in the work of Hohenberg and Kohn will be examined in the following.

The *first Hohenberg–Kohn theorem* 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). Since the original proof is enlightening and simple, it will be reproduced here. Assume two different system potentials, $v_a(\mathbf{r})$ and $v_b(\mathbf{r})$. If they differ by more than an additive constant, they must give rise to two different ground states in the Schrödinger equation, $\Psi_a$ and $\Psi_b$. Let us assume the states to be non-degenerate and that they both have the same electronic density $n(\mathbf{r})$. Let $\hat{\mathrm{H}}_a$ be the Hamiltonian for the system with potential $v_a(\mathbf{r})$. Use the Rayleigh–Ritz variational principle and the functional notation of Eq. (2.16) to get

$$E_a = \langle\Psi_a|\hat{\mathrm{H}}_a|\Psi_a\rangle < \langle\Psi_b|\hat{\mathrm{H}}_a|\Psi_b\rangle = F[\Psi_b] + V[v_a, n], \tag{2.21}$$

and in the same way,

$$E_b < F[\Psi_a] + V[v_b, n]. \tag{2.22}$$

If the two equations are added, the $F$ and $V$ terms on the right hand side can be recollected into $E$ terms,

$$E_a + E_b < E_b + E_a. \tag{2.23}$$

The last relation is a contradiction. The logical implication is: for systems without degenerate ground states, two different potentials cannot have the same ground state electron density.

The key point with the proof is that a ground state electron density uniquely determines the corresponding external potential of the system. This means all ground state properties of the system are also consequently determined, since in theory anything can be calculated from the external potential. Hence, we arrive at the main conclusion of the first Kohn–Sham theorem: *the electron density determines all ground state properties of a system.*

The ground state wave-function is also a ground state property of the system and can therefore be considered to be a functional of the ground state density $\Psi_0[n]$. The existence of the total energy functional $E_e[n]$ and an internal electronic energy functional $F[n]$ directly follows as

$$E_e[n] = \langle\, \Psi_0[n]\, |\hat{\mathrm{H}}_e|\, \Psi_0[n]\, \rangle \tag{2.24}$$

and

$$F[n] = F[\Psi_0[n]]. \tag{2.25}$$

The notation $\Psi_0[n]$ explicitly points out that the ground state is assumed to be non-degenerate (because the notation does not specify which one of the degenerate $\Psi_0$ the functional refers to). It is not very hard to reformulate the proof to lift the requirement of a non-degenerate ground state[17], roughly by reasoning in terms of 'any one of the degenerate ground state wave-functions'.

## 2.5 The Constrained Search Formulation

After the initial work of Hohenberg and Kohn it was discovered how an explicit but somewhat artificial definition of the internal electronic energy $F[n]$ can be constructed[18–21]:

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{\mathrm{T}} + \hat{\mathrm{U}} | \Psi \rangle, \tag{2.26}$$

where the minimum is taken over all many-electron wave-functions $\Psi$ with the specified electron density $n$. The existence of an explicit definition simplifies the derivation of the fundamental theorems. This formulation of DFT is called the *constrained search formulation*. It does not require any assumptions of a non-degenerate ground state.

## 2.6 The Second Hohenberg–Kohn Theorem

The *second Hohenberg–Kohn theorem* reworks the Rayleigh–Ritz variational principle into a *DFT variational principle* for the total energy combination[†] $F[n] + V[v,n]$. The constrained search formalism makes the proof straightforward. The Rayleigh–Ritz variational principle Eq. (2.12) can be split into two separate minimizations,

$$E_0 = \min_{\Psi} \langle \Psi | \hat{\mathrm{H}}_e | \Psi \rangle = \min_{n} \min_{\Psi \to n} \langle \Psi | \hat{\mathrm{T}} + \hat{\mathrm{U}} + \hat{\mathrm{V}} | \Psi \rangle = \min_{n} (F[n] + V[v,n]), \quad (2.27)$$

where the notation is as explained in Eq. (2.26). The many-electron problem thus has been rewritten into what looks like a straightforward minimization in a three-dimensional quantity $n(\mathbf{r})$, yet no approximations relative to a solution of the many-electron Schrödinger equation Eq. (2.4) have been made. The problem left is 'only' that the definition of $F[n]$ in Eq. (2.26) is very unpractical. It re-introduces a minimization over many-electron wave-functions that we set out to avoid. Hence, if one were to perform a constrained search in practice, one would not gain anything over a brute force wave-function based approach. In conclusion, the results just described provide a formal footing for DFT in that the existence and possible use of a universal internal electronic energy functional $F[n]$ have been established. But so far we have presented little hint on how to actually obtain it. There is no obvious way to create a practical 'approximative constrained search'.

## 2.7 $v$-Representability

The original work of Hohenberg and Kohn[2] assumed that the search for the density that minimizes the energy was only over densities that correspond to existing external potentials. A density that has such a corresponding external potential is called *$v$-representable*. The problem is that there is no known practical way to restrict a search to be over only $v$-representable densities.

In the constrained search formulation as presented in Eqs. (2.26) and (2.27) the electron densities are not assumed to be $v$-representable. The Rayleigh–Ritz variational principle is defined to work for all $N$-electron antisymmetric wave-functions, so the only requirement on the electron density is that it must correspond to such a wave-function; it must be *$N$-representable*. It has been shown that any 'reasonable' electron density fulfills the $N$-representability requirement[22].

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[†] Note the formal difference between $F[n] + V[v,n]$, and the form shown to exist in Eq. (2.24), $E_e[n] = F[n] + V[v(\mathbf{r},[n]),n]$. The former has an explicit dependence on the real external potential $v(\mathbf{r})$ of the system, whereas the latter uses the external potential that corresponds to the inserted density, $v(\mathbf{r},[n])$. These two external potentials are the same only when the true ground state electron density is used. It is obvious that we need to use $F[n] + V[v,n]$, and not $E_e[n]$, in a variational principle: 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 state that $E[\tilde{n}] > E[n]$, since all trial densities should give higher energies than the true density does. 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 fallacy; the explicit dependence on the real external potential $v(\mathbf{r})$ differentiates between the two cases.

The solution to the $v$-representability problem presented by the constrained search formulation means that there is no formal problem with the Hohenberg–Kohn theorems. The issue of $v$-representability is nevertheless still relevant in the context of more practical definitions of the $F[n]$ functional than the one in Eq. (2.26). Formally one would need to verify the behavior of approximations of $F[n]$ for non $v$-representable densities (e.g., if they approximate the constrained search $F[n]$ for such densities), but this issue has not been reported to cause practical problems for DFT calculations.

It is still an active field of research to determine the criteria for a density to be $v$-representable.

## 2.8 Density Matrix Theory

It has been established above that the internal electronic energy $F = T + U$ can be reformulated as a density functional, but it is not obvious how to do so. As a first step, *density matrices* can be used to express it as a functional of simpler quantities than the full electronic wave-function $\Psi_e$. The relation between the electron density and the many-electron wave-function in Eq. (2.14) can be generalized into the *first order spinless density matrix*,

$$n_1(\mathbf{r}', \mathbf{r}) = N \iint \dots \int \Psi_e(\mathbf{r}'\sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi_e^*(\mathbf{r}\sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\sigma_1 d\mathbf{x}_3 \dots d\mathbf{x}_N. \tag{2.28}$$

The kinetic energy can now be expressed as[6]

$$T[n_1] = -\left(\frac{\hbar^2}{2m_e}\right) \int \left[\nabla_{\mathbf{r}}^2 n_1(\mathbf{r}', \mathbf{r})\right]_{\mathbf{r}'=\mathbf{r}} d\mathbf{r}. \tag{2.29}$$

Another possible generalization of the density is the *pair density*

$$n_2(\mathbf{r}', \mathbf{r}) = N\frac{(N-1)}{2} \iint \dots \int \left|\Psi_e(\mathbf{r}\sigma_1, \mathbf{r}'\sigma_2, \mathbf{x}_3, \dots, \mathbf{x}_N)\right|^2 d\sigma_1 d\sigma_2 d\mathbf{x}_3 \dots d\mathbf{x}_N. \tag{2.30}$$

The internal potential energy becomes[6]

$$U[n_2] = \left(\frac{e_c^2}{4\pi\epsilon_0}\right) \iint \frac{n_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{2.31}$$

One may think the hard work involved in the construction of pure density functionals could be avoided if one instead keeps the density matrices and uses a density matrix minimization principle. The problem with such a minimization is that any trial density matrix must correspond to an antisymmetric many-electron wave-function $\Psi_e$, i.e., the trial density matrices must be $N$-representable. It turns out to be very hard to restrict the search to be over only $N$-representable density matrices.

## Chapter 3

# The Kohn–Sham Scheme

> *The real voyage of discovery consists not in seeking new landscapes, but in having new eyes.*
>
> Marcel Proust

In the previous chapter we arrived at a general minimization principle for finding the ground state electronic energy of a system. The scheme was not useful in practice, since only an abstract definition of the functional for the kinetic and interaction energies of the electrons $F[n]$ was available. In the present chapter we discuss the elaborate scheme of Kohn and Sham[3] to compute the dominating part of $F[n]$.

## 3.1 The Auxiliary Non-interacting System

Soon after the original Hohenberg–Kohn paper on DFT, Kohn and Sham[3] proposed a method for computing the main contribution to the kinetic energy functional to good accuracy, the *Kohn–Sham method*. Their idea was to rewrite the system of many interacting electrons as a system of *non-interacting Kohn–Sham particles*. These particles behave as non-interacting electrons[†].

The first step is to divide the internal electronic energy functional $F[n]$ into three parts,

$$F[n] = T_s[n] + J[n] + E_{xc}[n]. \tag{3.1}$$

Here $T_s[n]$ is the *non-interacting kinetic energy*, i.e., the kinetic energy of a system of non-interacting Kohn–Sham particles with particle density $n$; $J[n]$ is the electrostatic energy of a classical repulsive gas as it was defined in the section about Thomas–Fermi theory,

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[†] With non-interacting electrons we refer to fictitious particles that do not interact with each other by Coulomb forces, i.e., the internal potential energy $\hat{U} = 0$. The particles are still regarded as indistinguishable fermions. The indistinguishability of the Kohn–Sham particles is further commented on in relation to Eq. (3.11).

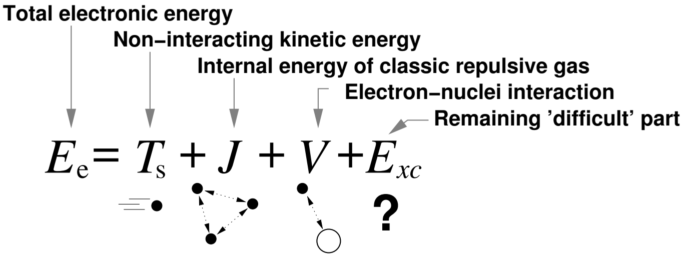
Total electronic energy
Non−interacting kinetic energy
Internal energy of classic repulsive gas
Electron−nuclei interaction
Remaining 'difficult' part
$E_e = T_s + J + V + E_{xc}$
?

**Figure 3.1.** The different contributions to the energy in the Kohn–Sham scheme.

Eq. (2.18); and $E_{xc}[n]$ is the *exchange-correlation energy*, which is *defined* to make the relation exact;

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

Hence, $E_{xc}[n]$ is the component of $F[n]$ which takes care of the non-classical part of the potential and kinetic energy related to electron interactions. The electronic energy is now divided into four parts, cf. Fig. 3.1.

The DFT variational principle for the ground state electronic energy $E_0$ in Eq. (2.27) can be expressed in the new quantities,

$$E_0 = \min_n (T_s[n] + J[n] + E_{xc}[n] + V[v, n]). \tag{3.3}$$

In the language of variational calculus this energy minimization can be rewritten as a *stationary condition*[†] for the electron density

$$\frac{\delta T_s[n]}{\delta n} + \frac{\delta E_{xc}[n]}{\delta n} + \frac{\delta J[n]}{\delta n} + \frac{\delta V[v, n]}{\delta n} = 0. \tag{3.4}$$

Now we look at what the above relations correspond to when DFT is applied to the system of the non-interacting Kohn–Sham particles. The DFT variational principle becomes

$$E_s = \min_n (T_s[n] + V[v_{\text{eff}}, n]), \tag{3.5}$$

where we use $E_s$ as the ground state energy of the system of Kohn–Sham particles and $v_{\text{eff}}(\mathbf{r})$ is the potential in which they move. The stationary condition becomes

$$\frac{\delta T_s[n]}{\delta n} + \frac{\delta V[v_{\text{eff}}, n]}{\delta n} = 0. \tag{3.6}$$

---

[†] The way the minimization is expressed in the formalism of variational calculus as a stationary condition has some parallels to the search of a minimum of an ordinary function. It is well known how the latter leads to the condition that the derivative should be zero at the point of extremum.

A comparison between the stationary conditions of the interacting and non-interacting systems, Eqs. (3.4) and (3.6), shows that *the same* stationary $n(\mathbf{r})$ is described if

$$\frac{\delta V[v_{\text{eff}}, n]}{\delta n} = \frac{\delta E_{xc}[n]}{\delta n} + \frac{\delta J[n]}{\delta n} + \frac{\delta V[v, n]}{\delta n}. \tag{3.7}$$

The functional derivatives are evaluated on both sides to give

$$v_{\text{eff}}(\mathbf{r}) = v_{xc}(\mathbf{r}) + \left(\frac{e_c^2}{4\pi\epsilon_0}\right) \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v(\mathbf{r}), \tag{3.8}$$

where the *exchange-correlation potential* $v_{xc}(\mathbf{r})$ is defined as

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n}. \tag{3.9}$$

The definition of $v_{\text{eff}}$ Eq. (3.8) is inserted into the expression for the $V[v, n]$ functional Eq. (2.15) to derive a relation between the energies of the two systems. By identifying the terms in the relation, the result can be written

$$E_0 = E_s - J[n] + E_{xc}[n] - V[v_{xc}, n]. \tag{3.10}$$

In conclusion, it has been established that *the non-interacting Kohn–Sham particle system with $v_{\text{eff}}$ as given in Eq. (3.8) has the same ground state density as the system of fully interacting electrons*. The energies of the two systems are closely related through Eq. (3.10). An auxiliary view of a system of interacting electrons is therefore promoted—the view of non-interacting Kohn–Sham particles in an *effective potential* $v_{\text{eff}}$. The potential $v_{\text{eff}}$ is formally expressed in Eq. (3.8) as a functional derivative of the unknown, difficult, part of the energy that corresponds to non-classical electron interactions, the exchange-correlation energy $E_{xc}$. The non-interacting auxiliary view is a central result for the Kohn–Sham scheme. In the following we will explore how to solve the auxiliary problem, and show that the non-interacting kinetic energy $T_s[n]$ can be calculated with much less effort than needed in a brute force constrained search.

## 3.2 Solving the Orbital Equation

The point of the previous section was that one can perform a minimization of the energy of an auxiliary problem of non-interacting Kohn–Sham particles Eq. (3.5) instead of a many-electron energy minimization Eq. (3.3). The non-interacting particle problem can be handled in a very direct way, through the explicit solution of the (in this case) separable Schrödinger equation. Separation leads to the *Kohn–Sham orbital equation*, which determines the one-particle *Kohn–Sham orbitals* $\phi_i(\mathbf{r})$ and the *Kohn–Sham orbital energies* $\epsilon_i$,

$$-\left(\frac{\hbar^2}{2m_e}\right) \nabla^2 \phi_i(\mathbf{r}) + v_{\text{eff}}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}). \tag{3.11}$$

Actual one-particle wave-functions are constructed as combinations of position dependent parts and *spin functions*, $\psi_i(\mathbf{r},\sigma) = \phi_i(\mathbf{r})\chi_i(\sigma)$. The ground state wave-function of the many-independent particle system is a *Slater determinant*[†] $\Psi = 1/\sqrt{N!}\,\det_{ij}\psi_j(\mathbf{r}_i,\sigma_i)$. The many-particle wave function is inserted in the usual expression for the electron density Eq. (2.14) to give the particle density,

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2, \tag{3.12}$$

where the sum is taken over all occupied spin-states $i$ (i.e., two per fully occupied orbital). For the usual zero temperature non–spin-polarized case the count of the occupied states starts with the orbitals of lowest energy and progress upwards until all $N$ electrons have been accounted for.[‡] The total energy of the system is

$$E_s = \sum_i \epsilon_i. \tag{3.13}$$

Common matrix methods can be used to solve the Kohn–Sham orbital equation.

Equations (3.8)–(3.13) are the *Kohn–Sham equations*, which are at the heart of any Kohn–Sham based DFT computer program. These equations cannot be straightforwardly solved from top down, because $v_{\text{eff}}$ in Eq. (3.9) requires the unknown electron density. However, in the previous section is was argued that the existence of a minimization principle over densities Eq. (3.5) means that the correct electron density $n(\mathbf{r})$ fulfills a stationary condition, Eq. (3.6). Such a stationary $n(\mathbf{r})$ can be found by an iterative scheme which works towards self-consistency. First, start with a trial density constructed in some way. Then repeat these steps until self-consistency is achieved:

1. Insert the density in Eq. (3.9) to produce an effective potential.
2. Solve the Kohn–Sham orbital equation Eq. (3.11).
3. Compute a new Kohn–Sham particle density from the Kohn–Sham orbitals through Eq. (3.12).

The result is an electron density $n(\mathbf{r})$ that is likely to be the stationary $n(\mathbf{r})$ that minimizes $E_s$ in Eq. (3.5). A schematic outline of the procedure is shown in Fig. 3.2.

---

[†] As previously noted, we take the Kohn–Sham particles to behave similar to non-interacting but indistinguishable electrons. The many-electron ground state wave-function for indistinguishable electrons is known to be in Slater determinant form, and thus the same applies to the Kohn–Sham particles. However, with the internal potential energy $\hat{\text{U}} = 0$ there is in fact no difference between the Hamiltonians obtained when either a Slater determinant or just a product wave-function are inserted. Furthermore, the density for *distinguishable* 'independent' particles in orbitals $\phi_i$ is also $\sum_i |\phi_i|^2$. In the present context it therefore turns out not to be an important distinction whether the Kohn–Sham particles are regarded as indistinguishable or not. Terminology belonging to both views are present in literature, e.g., compare Refs. 6 and 8.

[‡] It has been discussed that there may exist an interacting electron system with a density that cannot be constructed as the lowest $N$ eigenstates of a system of non-interacting Kohn–Sham particles[20], but there are no reports that such densities generate problems in actual DFT calculations. Furthermore, for practical reasons it is common in computer implementations to occupy the eigenstates according to a Fermi–Dirac distribution for a small temperature rather than strictly using the lowest eigenstates.

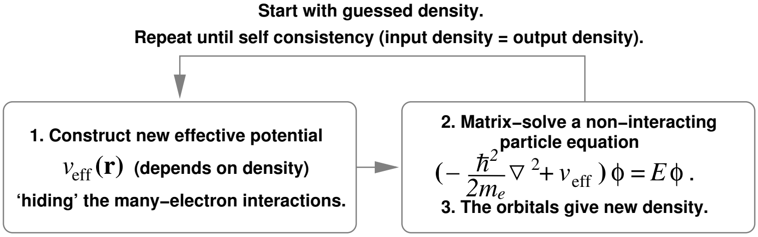
Start with guessed density.
Repeat until self consistency (input density = output density).
1. Construct new effective potential
$v_{\text{eff}}(\mathbf{r})$ (depends on density)
'hiding' the many-electron interactions.
2. Matrix-solve a non-interacting particle equation
$(-\frac{\hbar^2}{2m_e}\nabla^2 + v_{\text{eff}})\,\phi = E\,\phi\,.$
3. The orbitals give new density.

**Figure 3.2.** Schematic representation of the self-consistent solution of the Kohn–Sham equations.

## 3.3 The Kohn–Sham Orbitals

It is common to think about bonding between atoms and molecules in terms of the interaction between electrons in electronic orbitals; but there are no such orbitals inherent to the many-electron system itself. The single-particle orbitals referred to are introduced as a component of the Hartree–Fock[§] picture of electronic structure. The Kohn–Sham scheme provides an alternative, and in theory exact, orbital theory.

Despite the possibility of regarding the Kohn–Sham method as an exact orbital theory, it is important to realize that the orbitals originate from a system auxiliary to the many-electron system. The connection between the interacting and non-interacting systems is only through the systems having the same particle density. In particular, the auxiliary system has not been created with any 'correct' orbital description of the many-electron system in mind. Thus one should not anticipate any strict physical significance of the orbitals. In the same way one should not expect any simple interpretation of the Kohn–Sham orbital energies $\epsilon_i$ in Eq. (3.11). It has long been believed that the energy of the highest occupied Kohn–Sham orbital is the negative of the exact many-electron ionization energy[23,24], but more recently this claim has been called into question[25–29].

Even though a simple physical interpretation of the Kohn–Sham orbitals and energies is missing, it is still quite common to take them as approximations for the Hartree–Fock orbitals and energies. The results are usually surprisingly good. Still, one should keep in mind that to comment on DFT's relative 'success' or 'failure' based on how well the Kohn–Sham orbitals reproduce the Hartree–Fock orbital band structure is theoretically misguided. It is worth pointing out that DFT's well known 'failure' to reproduce band gap energies in semiconductors may only be a failure of the habit of using Kohn–Sham orbitals as approximations for Hartree–Fock orbitals.

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[§] The *Hartree–Fock method* approximates the solution to the many-electron problem by assuming that the many-electron wave-function can be written on the form of a Slater determinant of single particle orbitals. The theory can be made exact by completing the basis in which the wave-function is expressed with Slater determinants of orbitals of successively higher energies; this extension is called *configuration interaction*. The Hartree–Fock method is itself an extension of the *Hartree method* where the many-electron wave-function is assumed to be a simple product of one-electron orbitals. The Hartree assumption means that the electrons are described as purely independent non-interacting particles.

## Chapter 4

# EXCHANGE AND CORRELATION

> *When you have come to the edge of all light that you know and are about to drop off into the darkness of the unknown, faith is knowing one of two things will happen: there will be something solid to stand on or you will be taught to fly.*
>
> Patrick Overton

The DFT core theory has left us with one specific goal: to construct a density functional for the internal electronic energy $F[n]$ that is as accurate as possible. The previous chapter gave a method for the calculation of the largest contributions to this functional, the non-interacting kinetic energy $T_s[n]$ and the electrostatic energy of a classical repulsive gas $J[n]$. In this chapter we turn to the last part that remains, the exchange-correlation energy $E_{xc}[n]$. This functional encompasses all the difficult quantum mechanical behavior of interacting electrons.

## 4.1 Decomposing the Exchange-Correlation Energy

In the previous chapter, the exchange-correlation energy was defined as the exact internal electronic energy of a many-body electron system $F[n]$ minus the contributions that now can be computed exactly, $T_s[n]$ and $J[n]$,

$$E_{xc}[n] = F[n] - T_s[n] - J[n] = (T[n] - T_s[n]) + (U[n] - J[n]). \tag{4.1}$$

In the last step, the expression is put on a form that shows explicitly how $E_{xc}$ is a sum of two more or less unrelated parts: the correction to the kinetic energy due to electron interactions $T[n] - T_s[n]$, and the correction to the electrostatic energy due to non-classical quantum mechanical interactions $U[n] - J[n]$.

It is clear that $E_{xc}$ in itself is not a 'local quantity' as it has no spatial coordinate dependence. It is equally affected by all changes throughout the system. To get an (arguably) semi-local quantity to work with, it is common to implicitly define the *exchange-correlation energy per particle* $\epsilon_{xc}([n];\mathbf{r})$ by

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}([n];\mathbf{r})d\mathbf{r}. \tag{4.2}$$

The quantity $\epsilon_{xc}([n];\mathbf{r})$ has a spatial dependence and is expected[4,5] to show some kind of 'locality', in the sense of being mostly dependent on the part of the electron density which is close to $\mathbf{r}$.

The implicit definition of the exchange-correlation energy per particle $\epsilon_{xc}([n];\mathbf{r})$ leaves us with a freedom of choice. Let $f(\mathbf{r})$ be a function that gives zero when integrated over $\mathbf{r}$. Given a valid $\epsilon_{xc}([n];\mathbf{r})$, an equally valid alternative can be constructed as $\epsilon_{xc}([n];\mathbf{r}) + f(\mathbf{r})/n(\mathbf{r})$. The freedom of choice for the exchange-correlation energy per particle is important for the subsystem functional approach and is discussed more in chapter 7 and paper 1 of part III.

## 4.2 The Adiabatic Connection

To enable the development of approximations for the exchange-correlation energy per particle $\epsilon_{xc}([n];\mathbf{r})$, we first consider how to formulate it exactly in quantities easier to handle than the many-electron wave-function $\Psi_e$. One approach would be to use the quantities of the density matrix theory of section 2.8; the first order spinless density matrix Eq. (2.28) and the pair density Eq. (2.30). However, an alternative approach is pursued in this section, the trick of *coupling constant integration* in the *adiabatic connection*[6,30–32]. In the next section the results found here will be used to derive a composite expression for the exchange-correlation energy that involves a new 6-dimensional quantity with a rather intricate relation to the pair density, the exchange-correlation hole.

For a real system, described by $\hat{\mathrm{H}}_e$ with electron density $n(\mathbf{r})$, one can define a scaled Hamiltonian $\hat{\mathrm{H}}_\lambda$ where the strength of the electronic interactions is scaled down by a factor $0 < \lambda < 1$,

$$\hat{\mathrm{H}}_\lambda = \hat{\mathrm{T}} + \lambda\hat{\mathrm{U}} + \hat{\mathrm{V}}_\lambda. \tag{4.3}$$

The potential function in the potential energy operator $\hat{\mathrm{V}}_\lambda$ is chosen as in Kohn–Sham theory[†] to make the system's density $n$ be the same for all values of $\lambda$. Thus, there exists a continuum of Hamiltonians, ranging from the Kohn–Sham system at $\lambda = 0$ to the real interacting system at $\lambda = 1$. For each $\lambda$, the scaled Hamiltonian $\hat{\mathrm{H}}_\lambda$ has a corresponding ground state many-particle wave-function $\Psi_\lambda$.

The many-particle wave-function gives the total internal electronic energy as a normal expectation value,

$$F_\lambda = \langle\Psi_\lambda|\hat{\mathrm{T}} + \lambda\hat{\mathrm{U}}|\Psi_\lambda\rangle. \tag{4.4}$$

---

[†] The here given derivation of the adiabatic connection assumes the electronic density to be of a nature that allows potential functions to be constructed to keep it constant for different coupling strengths, i.e., that the density is $v$-representable; see e.g. Ref 6 for more information.

The fully interacting and the non-interacting cases are recognized as

$$F_1[n] = F[n] = T[n] + U[n] \quad \text{and} \quad F_0[n] = T_s[n]. \tag{4.5}$$

The definition of the (fully interacting) exchange-correlation energy Eq. (4.1) is now easily rewritten

$$E_{xc} = U[n] - J[n] + T[n] - T_s[n] = F_1[n] - F_0[n] - J[n] \tag{4.6}$$

$$= \int_0^1 \frac{\partial F_\lambda}{\partial \lambda} d\lambda - J[n]. \tag{4.7}$$

The derivative in the last step can be obtained using the Hellman–Feynman theorem of quantum mechanics. It is found that

$$\frac{\partial F_\lambda}{\partial \lambda} = \langle \Psi_\lambda | \hat{\mathrm{U}} | \Psi_\lambda \rangle. \tag{4.8}$$

The expression for the exchange-correlation energy is simplified by defining the *potential energy of exchange-correlation* at coupling strength $\lambda$ as

$$U_{xc}^\lambda = \langle \Psi_\lambda | \hat{\mathrm{U}} | \Psi_\lambda \rangle - J[n]. \tag{4.9}$$

Thus we arrive at the adiabatic connection formula

$$E_{xc} = \int_0^1 U_{xc}^\lambda d\lambda. \tag{4.10}$$

An interesting observation can be made[33]: the integral in Eq. (4.10) explicitly only involves the internal potential energy part of the exchange-correlation energy. The kinetic energy part is therefore generated, in effect, by the $\lambda$ integration.

## 4.3 The Exchange-Correlation Hole

The adiabatic connection formula Eq. (4.10) was expressed in the potential energy of exchange-correlation $U_{xc}^\lambda$. The quantity $U_{xc}^\lambda$ involves the full many-particle wave-function. In the following we work towards a more manageable expression by expressing the adiabatic connection formula in the pair-density. The many-particle wave-function $\Psi_\lambda$ is inserted into the ordinary wave-function expression for the pair density Eq. (2.30) to generate $n_2^\lambda(\mathbf{r}', \mathbf{r})$. To further simplify the formulas, define the *averaged pair density*

$$\overline{n}_2(\mathbf{r}', \mathbf{r}) = \int n_2^\lambda(\mathbf{r}', \mathbf{r}) d\lambda. \tag{4.11}$$

The adiabatic connection for the exchange-correlation energy Eq. (4.10), when expressed using the averaged pair density, becomes

$$E_{xc} = \left( \frac{e_c^2}{4\pi\epsilon_0} \right) \iint \frac{\overline{n}_2(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - J[n]. \tag{4.12}$$

The final step is to define the *exchange-correlation hole* $\hat{n}_{xc}(\mathbf{r}',\mathbf{r})$ from

$$\overline{n}_2(\mathbf{r}',\mathbf{r}) = \frac{1}{2}\Big(n(\mathbf{r})\hat{n}_{xc}(\mathbf{r}',\mathbf{r}) + n(\mathbf{r}')n(\mathbf{r})\Big) \tag{4.13}$$

to get the expression

$$E_{xc} = \frac{1}{2}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\iint \frac{n(\mathbf{r})\hat{n}_{xc}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{4.14}$$

This final expression may not look very useful at first. The definition of $\hat{n}_{xc}(\mathbf{r}',\mathbf{r})$ is obviously complicated, involving pair densities created from a continuum of exact solutions to many-particle problems. However, the exchange-correlation hole is a useful tool for reasoning. The definition of $\hat{n}_{xc}(\mathbf{r}',\mathbf{r})$ is deliberately chosen to put the expression for $E_{xc}$ in Eq. (4.14) on the form of a classical Coulomb interaction integral. Hence, the exchange-correlation energy $E_{xc}$ can be interpreted as the result of a simple electrostatic interaction between electrons and their corresponding exchange-correlation holes. The name 'exchange-correlation hole' is motivated by the idea that the quantity represents a 'hole' created in the electron density as an electron at $\mathbf{r}$ 'pushes away' other electrons. The interpretation of the $\hat{n}_{xc}$ quantity as an electron hole is further rationalized by the exact *exchange-correlation hole sum rule*

$$\int \hat{n}_{xc}(\mathbf{r},\mathbf{r}')d\mathbf{r}' = -1. \tag{4.15}$$

It means that the 'size' of the hole equals that of the electron to which the hole belongs. The definition of $\hat{n}_{xc}(\mathbf{r}',\mathbf{r})$ may seem so complicated that it never could be used for actual calculations, but it turns out to be possible to compute numerical values for simple systems through Monte Carlo techniques[34–38]. In section 5.10 the definition is also used in a very practical way to motivate hybrid functionals.

Exchange-correlation holes alternative to $\hat{n}_{xc}$ can be defined. Any function $n_{xc}$ that gives the total exchange-correlation energy when integrated as in Eq. (4.14) is a 'delocalized' *unconventional exchange-correlation hole* $n_{xc}$. This is the same kind of freedom of choice as was discussed for the exchange-correlation energy per particle. By integration by parts or by the addition of a function whose integral is zero in Eq. (4.14) one arrives at some alternative $n_{xc}$.

## 4.4 The Exchange-Correlation Energy Per Particle

We now have the theoretical framework needed for defining the *local* and *conventional exchange-correlation energy per particle* $\hat{\epsilon}_{xc}([n];\mathbf{r})$. This is the specific choice of $\epsilon_{xc}([n];\mathbf{r})$ one gets from the definition of the exchange-correlation energy per particle, Eq. (4.2), and the relation for $E_{xc}$ expressed in $\hat{n}_{xc}$, Eq. (4.14),

$$\hat{\epsilon}_{xc}([n];\mathbf{r}) = \frac{1}{2}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\int \frac{\hat{n}_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{4.16}$$

Some authors[1,5] introduce a notation to stress that they work with the uniquely defined choice of $\hat{\epsilon}_{xc}([n];\mathbf{r})$—the *inverse radius of the exchange-correlation hole* $R_{xc}^{-1}([n];\mathbf{r})$. It is defined with no freedom of choice,

$$R_{xc}^{-1}([n];\mathbf{r}) = -\int \frac{\hat{n}_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{4.17}$$

$$\hat{\epsilon}_{xc}([n];\mathbf{r}) = -\frac{1}{2}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)R_{xc}^{-1}([n];\mathbf{r}). \tag{4.18}$$

## 4.5 Separation of Exchange and Correlation

It is common to divide the exchange-correlation energy $E_{xc}$ into separate *exchange energy* $E_x$ and *correlation energy* $E_c$ parts. Basically, the separation continues the trend to part quantities that can be explicitly formulated from 'the rest'. The explicit expression that defines $E_x$, and therefore also defines this division, will be given in the next section. Separate *exchange* $\epsilon_x([n];\mathbf{r})$ and *correlation energies per particle* $\epsilon_c([n];\mathbf{r})$ are defined as for the combined exchange-correlation energy Eq. (4.2),

$$E_x[n] = \int n(\mathbf{r})\epsilon_x([n];\mathbf{r})d\mathbf{r}, \tag{4.19}$$

$$E_c[n] = \int n(\mathbf{r})\epsilon_c([n];\mathbf{r})d\mathbf{r}, \tag{4.20}$$

where

$$E_{xc}[n] = E_x[n] + E_c[n]. \tag{4.21}$$

It should be obvious that one has the same freedom of choice for the separate $\epsilon_x$ and $\epsilon_c$ parts as for the compound $\epsilon_{xc}$ (i.e., any function that when integrated gives zero can be added to the integrals).

## 4.6 The Exchange Energy

The exchange part $E_x$ is *defined* through *one possible choice* of $\epsilon_x$; the *local* and *conventional exchange energy per particle* $\hat{\epsilon}_x([n];\mathbf{r})$,

$$\hat{\epsilon}_x([n];\mathbf{r}) = \frac{1}{2}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\int \frac{\hat{n}_x(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{4.22}$$

$$\hat{n}_x(\mathbf{r},\mathbf{r}') = -\frac{1}{2}\frac{|n_1(\mathbf{r},\mathbf{r}')|^2}{n(\mathbf{r})}. \tag{4.23}$$

Here we have also defined the *exchange hole* $\hat{n}_x(\mathbf{r},\mathbf{r}')$. The first-order spinless density matrix $n_1(\mathbf{r},\mathbf{r}')$, as defined in Eq. (2.28), takes a particularly simple form with the Kohn–Sham (Slater determinant) many-particle wave-function,

$$n_1(\mathbf{r},\mathbf{r}') = \sum_i \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}'), \tag{4.24}$$

where the sum is taken over all occupied spin-states $i$ (i.e., two per fully occupied orbital). The exchange hole fulfills the *exchange hole sum rule*,

$$\int \hat{n}_x(\mathbf{r}, \mathbf{r}')d\mathbf{r}' = -1. \tag{4.25}$$

Furthermore, it follows directly from Eq. (4.23) that the exchange hole is negative definite; the *non-positivity constraint*,

$$\hat{n}_x(\mathbf{r}, \mathbf{r}') \leq 0, \quad \forall\, \mathbf{r}, \mathbf{r}'. \tag{4.26}$$

The integration Eq. (4.19) of the above definition of $\epsilon_x$ defines the total exchange energy $E_x$ (and therefore also defines the separation of the exchange-correlation energy $E_{xc}$ in exchange $E_x$ and correlation $E_c$ parts). The total exchange energy has a very useful *exchange scaling relation*[39] that describes its behavior when presented with a density scaled by a scalar $\gamma$;

$$E_x[n_\gamma] = \gamma E_x[n] \quad \text{for} \quad n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r}). \tag{4.27}$$

The definition of the exchange energy can be included in an alternative Kohn–Sham scheme capable of an exact treatment of exchange[3] in a Hartree–Fock-like procedure. However, the non-local dependence on orbitals makes the equations significantly harder to solve. A much more common way of including exact exchange in DFT calculations is instead to use the exchange expressions above as the exchange part of a regular DFT functional. Since that functional is not really a density functional, the effective potential $v_{\text{eff}}$ cannot be obtained as a direct functional derivative. Instead, one typically produces $v_{\text{eff}}$ through an indirect procedure, the optimized effective potential (OEP) method[40–42]. Note that exact exchange methods does not universally improve the total exchange-correlation energy. Simultaneous approximation of exchange and correlation can be beneficial in that it enables a cancellation of errors between exchange and correlation that is not possible in exact exchange calculations.

The exchange part of the exchange-correlation energy should formally be called the Kohn–Sham exchange and it is not the same as the Hartree–Fock exchange. The definitions both looks like Eq. (4.22), but the Kohn–Sham exchange Eq. (4.22) uses the Kohn–Sham orbitals which are not the same as the Hartree–Fock orbitals (cf. section 3.3).

Similar to the exchange-correlation hole, exchange holes alternative to $\hat{n}_x$ can be defined. Any function $n_x$ that gives the total exchange energy when inserted and integrated in Eqs. (4.19) and (4.22) is an *unconventional exchange hole*.

## 4.7 The Correlation Energy

When the exchange part is subtracted from the exchange-correlation energy per particle, the remaining part is the *correlation energy per particle*,

$$\hat{\epsilon}_c([n]; \mathbf{r}) = \frac{1}{2}\left(\frac{e_c^2}{4\pi\epsilon_0}\right) \int \frac{\hat{n}_c(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{4.28}$$

$$\hat{n}_c(\mathbf{r}, \mathbf{r}') = \hat{n}_{xc}(\mathbf{r}, \mathbf{r}') - \hat{n}_x(\mathbf{r}, \mathbf{r}'), \tag{4.29}$$

where the *correlation hole* $\hat{n}_c(\mathbf{r}, \mathbf{r}')$ is defined by the last relation. By comparing the sum rule for exchange-correlation Eq. (4.15) with the one for exchange Eq. (4.25), the *correlation hole sum rule* follows,

$$\int \hat{n}_c(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 0. \tag{4.30}$$

Similar to the exchange-correlation and separate exchange holes, correlation holes alternative to $\hat{n}_c$ can be defined. Any function $n_c$ that gives the total correlation energy when integrated as in Eqs. (4.20) and (4.28) is an *unconventional correlation hole*.

## Chapter 5

# FUNCTIONAL DEVELOPMENT

> *It is the mark of an educated mind to rest satisfied with the degree of precision which the nature of the subject admits and not to seek exactness where only an approximation is possible.*
>
> Aristotle

In previous chapters all the energy contributions to the total many-electron energy have been discussed. It has been made clear that the most difficult parts have been condensed into the exchange-correlation energy $E_{xc}$. A number of definitions and theoretical results for working with this quantity were presented in the last chapter. In this chapter we turn to the methods used for creating practical approximations.

## 5.1 Locality

Approximations of the exchange-correlation energy per particle $\epsilon_{xc}([n];\mathbf{r})$ are often characterized in terms of their 'locality'. Two forms of locality are present in this context, and in the literature different conventions are used, so the discussion easily becomes confusing. The two forms of locality are: 1) The specific conventional choice of exchange-correlation energy $\hat{\epsilon}_x([n];\mathbf{r})$, as defined in Eq. (4.16), is the 'local' choice. 2) The functional $\epsilon_x([n];\mathbf{r})$ can be a more or less *local functional* of the electron density. The meaning of "local functional" will be further explained in the following. The exchange-correlation energy $E_{xc}$ is given as an integration of $\epsilon_{xc}([n];\mathbf{r})$ together with the electronic density over the whole space. The locality of the functional describes to what extent the largest energy contribution in the integration comes from the parts of $n(\mathbf{r}')$ where $\mathbf{r}'$ is close to $\mathbf{r}$. If $\epsilon_{xc}$ is more or less independent of the distance $\mathbf{r}-\mathbf{r}'$, it is a very *non-local functional*.

To reiterate,

> An *approximation to the local exchange-correlation energy* is a functional that aims to approximate the specific local choice of the exchange-correlation energy per particle, $\hat{\epsilon}_x([n];\mathbf{r})$.
>
> A *local functional of the density* (or a *functional on local form*) is a functional $\epsilon_{xc}([n];\mathbf{r})$ that depends on the electronic density *only* at the local point $\mathbf{r}$. Thus it is a function, rather than a functional, of the electronic density: $\epsilon_{xc}([n];\mathbf{r}) = \epsilon_{xc}(n(\mathbf{r}))$. The assumption that the functional is on this form produces the local density approximation of section 5.2.
>
> A *semi-local functional of the density* (or a *functional on semi-local form* ) is a functional $\epsilon_{xc}([n];\mathbf{r})$ with a dependence on the electronic density $n(\mathbf{r}')$ mostly focused around $\mathbf{r}' = \mathbf{r}$. If the functional is assumed to be on this form, it can be expressed as a function of the electron density and its derivatives (i.e., the gradient of the electronic density etc.) These ideas lead to the generalized gradient approximations of section 5.5.

One can also create exchange-correlation functionals that are strictly not density functionals, but rather use quantities with a direct relation to the Kohn–Sham orbitals (cf. section 5.8). As long as such a functional is a *local functional of the Kohn–Sham orbitals*, most of the computational efficiency of the Kohn–Sham scheme remains.

## 5.2 The Local Density Approximation, LDA

The *local density approximation* (LDA) is the most straightforward approximation of the exchange-correlation energy. It was proposed already in the first works on DFT[2,3]. One arrives at this functional from the assumption that the exchange-correlation energy per particle is a local functional of the electron density.

A *uniform electron gas system* has a constant $v_{\text{eff}}$. The symmetry of this system requires the electron density to be constant $n(\mathbf{r}) = n^{\text{unif}}$. It also follows that the exchange-correlation energy per particle is constant in space and thus can be expressed as a function (not a functional) of the uniform density, $\hat{\epsilon}_{xc}^{\text{unif}}(n^{\text{unif}})$. To construct the local density approximation, one takes in each space point $\mathbf{r}$ the real system's electron density and inserts it into the uniform exchange-correlation per particle function,

$$\hat{\epsilon}_{xc}^{\text{LDA}}(n(\mathbf{r})) = \hat{\epsilon}_{xc}^{\text{unif}}(n(\mathbf{r})). \tag{5.1}$$

A schematic illustration is shown in Fig. 5.1.

It is straightforward to derive the exchange part of LDA. The Kohn–Sham orbitals for a constant effective potential are plane waves. When these orbitals are inserted into the definition of the exchange energy per particle Eqs. (4.22)–(4.24), the result is a constant exchange energy per particle $\hat{\epsilon}_x^{\text{unif}}$ and a uniform electron density $n^{\text{unif}}$. The expression for

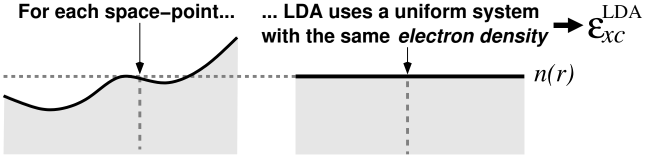
For each space-point...
... LDA uses a uniform system with the same *electron density*
$\varepsilon_{xc}^{\mathrm{LDA}}$
$n(r)$

**Figure 5.1.** The definition of the local density approximation.

$\hat{\epsilon}_x^{\mathrm{unif}}$ can then be rewritten as a function of the density $n^{\mathrm{unif}}$. Finally, the uniform density is replaced with a generic $n(\mathbf{r})$. The result is

$$\hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r})) = -\frac{3}{4\pi}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\left(3\pi^2 n(\mathbf{r})\right)^{1/3}. \tag{5.2}$$

It is common to express this in the dimensionless radius of the sphere that contains the charge of one electron,

$$r_s = \left(\frac{1}{a_0}\right)\left(\frac{3}{4\pi n(\mathbf{r})}\right)^{1/3}. \tag{5.3}$$

The result is

$$\hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r})) = -\frac{3}{4\pi}\left(\frac{9\pi}{4}\right)^{1/3}\left(\frac{e_c^2}{4\pi\epsilon_0 a_0}\right)\frac{1}{r_s}. \tag{5.4}$$

Exact LDA expressions for the correlation are only known in two limits. The first is the limit of high density and weak correlations[43–47]

$$\hat{\epsilon}_c^{\mathrm{LDA}}(n(\mathbf{r})) = \left(\frac{e_c^2}{4\pi\epsilon_0 a_0}\right)(c_0 \ln r_s + c_1 + c_2 r_s \ln r_s + c_3 r_s + \ldots), \quad r_s \ll 1. \tag{5.5}$$

The coefficients $c_0$, $c_2$, $c_3$, ... depend on the electron spin configuration. For a spin-unpolarized electron gas (equal number of spin up and spin down electrons) the constant $c_0$ was calculated[43] in 1950s; $c_0 = (1 - \ln 2)/\pi^2$. However, it was not until 1992 that $c_1$ was put on a form that could be evaluated to arbitrary precision[46], $c_1 \approx -0.046920$. Furthermore[44,45] $c_2 \approx 0.0092292$; and[47] $c_3 \approx -0.010$. There are also results available for a fully spin-polarized gas (where all electrons have the same spin).

The second known limit is that of low density and strong correlation[48–50],

$$\hat{\epsilon}_c^{\mathrm{LDA}}(n(\mathbf{r})) = \left(\frac{e_c^2}{4\pi\epsilon_0 a_0}\right)\left(\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \frac{d_2}{r_s^4} + \ldots\right), \quad r_s \gg 1. \tag{5.6}$$

It is common to use the knowledge of the form of this series when interpolation expressions are created, but usually one does not use calculated numerical values for the coefficients $d_0$, $d_1$, $d_2$, ... (A fit to data for intermediate densities gives values of the coefficients that can be seen as 'effective' power series coefficients).

Data for the correlation of the uniform electron gas for densities between the two known limits have been accurately computed by Monte Carlo methods[51]. Useful approximations of the correlation energy have been created by parameterization of the Monte Carlo data in a way that takes the known limits into account. There are three such parameterizations in popular use. Vosko, Wilk, and Nusair[52] presented in 1980 a careful analysis and parameterization. In 1981 Perdew and Zunger[53] independently created a parameterization in an appendix of a paper on how to correct the self-interaction error in DFT. Furthermore, in 1992 Perdew and Wang constructed another parameterization[45] based on the ideas of Vosko, Wilk, and Nusair. Note that none of these popular correlation parameterizations use the most accurate value available for $c_1$ in the high density limit Eq. (5.5). Section 9.2 and paper 3 discuss an alternative parameterization of LDA that uses an accurate value of $c_1$.

LDA was constructed as a suitable approximation for systems with a slowly varying electron density, but it was found remarkably successful for wider use. It is *still* used as the main functional for many solid state applications. At least three reasons have been put forward to explain why LDA is so successful:

1. The formal definition of the conventional exchange-correlation energy Eq. (4.14) can be used to show that a complete description of the ‘exact’ exchange-correlation hole is not needed, only its spherical average. It is found that LDA reproduces the spherical average of the real hole more accurately than it reproduces the real hole itself[54].

2. A number of constraints, which it is known that the exact exchange-correlation energy functional must fulfill, are also correctly reproduced by LDA, e.g., the sum rule Eq. (4.15).

3. LDA is based on a real physical model system, the uniform electron gas. Both exchange and correlation are reproduced *exactly* when the functional is applied to this model system. The fact that a physical model is used, and that exchange and correlation are treated in the same way, leads to *compatible exchange and correlation*. When exchange and correlation are approximated in this consistent way, their errors tend to cancel.

LDA has been a great success e.g. for applications in the solid state. However, there are cases where its accuracy is not sufficient. For example in the description of certain molecular system and for systems where explicit surfaces are present. In particular, LDA has a tendency to make chemical bindings much too strong, i.e., LDA overbinds.

## 5.3 The Exchange Refinement Factor

The electron density is a quantity of dimension $1/\text{length}^3$. For the exchange part one can [39], by dimensional analysis and the exchange scaling relation Eq. (4.27), conclude that the exact $\epsilon_x$ must depend on the bare density precisely as $n(\mathbf{r})^{1/3}$, just like LDA does. It is therefore common in the context of density functional development to define and work with the exchange *refinement factor* $F_x$,

$$\epsilon_x(\mathbf{r};[n]) = \hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r}))F_x. \tag{5.7}$$

The key point of working with $F_x$ instead of $\epsilon_x(\mathbf{r};[n])$ is that the LDA prefactor takes care of the known bare density dependence. It then follows that $F_x$ can only depend on *density-scale invariant dimensionless quantities*. Note that there is no known simple scaling relation for the correlation energy, so that part cannot be simplified in the same way.

In the next section we will discuss approximations to $\epsilon_x(\mathbf{r};[n])$ that use the gradient and Laplacian of the density. These density derivatives can be expressed on scale invariant form; the *dimensionless gradient*

$$s = \frac{|\nabla n(\mathbf{r})|}{2(3\pi^2)^{1/3}n^{4/3}(\mathbf{r})} \tag{5.8}$$

and the *dimensionless Laplacian*

$$q = \frac{\nabla^2 n(\mathbf{r})}{4(3\pi^2)^{2/3}n^{5/3}(\mathbf{r})}. \tag{5.9}$$

To verify that these definitions are indeed scale invariant, one can insert a density scaled as in Eq. (4.27) and observe that the scaling factors cancel. This is in contrast to, for example, the dimensionless $r_s$ parameter.

## 5.4 The Gradient Expansion Approximation, GEA

Already the earliest works of DFT[2,3] presented the idea of extending LDA in the form of a *gradient expansion approximation* (GEA). LDA uses only the local value of the electron density. The idea behind a GEA is to regard LDA as the first term in a power series expansion of $\epsilon_{xc}$ in the density's spatial variation (described by the derivatives of $n(\mathbf{r})$). The second-order GEA thus uses LDA plus the term of next lowest order in density variation, Taking all symmetries into account[2], this term is of order $O(\nabla^2)$ and the GEA is expressed in $s^2$ and $q$ as

$$\hat{\epsilon}_{xc} = \hat{\epsilon}_{xc}^{\mathrm{LDA}}(n(\mathbf{r})) + \left(\frac{e_c^2}{4\pi\epsilon_0 a_0}\right)\hat{A}_{xc}(n(\mathbf{r}))s^2 + \left(\frac{e_c^2}{4\pi\epsilon_0 a_0}\right)\hat{B}_{xc}(n(\mathbf{r}))q + \ldots, \tag{5.10}$$

where $\hat{A}_{xc}(n(\mathbf{r}))$ and $\hat{B}_{xc}(n(\mathbf{r}))$ are dimensionless functions (not functionals) of $n(\mathbf{r})$. It is also possible to eliminate the term proportional to the Laplacian by an integration by parts in the integral over $\epsilon_{xc}$ Eq. (4.2). However, note that then the known and local choice of $\hat{\epsilon}_{xc}$ is transformed into an unknown and non-local $\epsilon_{xc}$,

$$\epsilon_{xc} = \hat{\epsilon}_{xc}^{\mathrm{LDA}}(n(\mathbf{r})) + \left(\frac{e_c^2}{4\pi\epsilon_0 a_0}\right)A_{xc}(n(\mathbf{r}))s^2 + \ldots. \tag{5.11}$$

The exchange part of the GEA can be simplified by using the insights from the previous section: an LDA prefactor can be extracted to take care of all bare density dependence. The coefficients must then be scalar;

$$\hat{\epsilon}_x = \hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r}))\Big(1 + \hat{a}_x s^2 + \hat{b}_x q + ...\Big), \tag{5.12}$$

$$\epsilon_x = \hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r}))\Big(1 + a_x s^2 + ...\Big). \tag{5.13}$$

For the latter, transformed, expression one finds[55–57] $a_x = 10/81$. However, for the untransformed expression an explicit calculation of $\hat{\epsilon}_x$ for a model system in the limit of slowly varying electron densities shows that the suggested power expansion generally *does not exist* on the above form. This is further discussed in chapter 9 and paper 1 of part III.

For the correlation term, it is common to work with the density variation expressed in the *reduced density gradient* $t$ instead of $s$ (but the two are interchangeable),

$$t^2 = \frac{|\nabla n(\mathbf{r})|^2}{16[3/(\pi a_0^3 n)]^{1/3} n^{8/3}(\mathbf{r})}, \tag{5.14}$$

and write the expansion as,

$$\epsilon_c = \hat{\epsilon}_c^{\mathrm{LDA}}(n(\mathbf{r})) + \left(\frac{e_c^2}{4\pi\epsilon_0 a_0}\right) A_c(n(\mathbf{r}))t^2 + .... \tag{5.15}$$

Ma and Brueckner[58] calculated the value of the dimensionless function $A_c \approx 0.0667244$ in the $n \to \infty$ limit. Later an explicit expression for $A_c$ was derived[59–61] and numerically calculated for a number of values of the density.

The gradient coefficient for exchange $a_x = 10/81$ was not straightforward to establish. First Sham performed[62] a calculation based on the correlation methods of Ma and Brueckner[58] and obtained a value of $7/81$. Another calculation of Gross and Dreizler[63] confirmed the same result; but empirical results[64] indicated that the value was too low. Antoniewicz and Kleinman obtained $10/81$[55], and after some suggestions of Perdew and Wang[65], Kleinman and Lee[56] numerically demonstrated that the cause of the confusion was an order of limits problem between the Yukawa screening factor $\bar{k}_{\mathrm{Y}}$ and the wave vector of the density variation $K$. The problem is nicely exemplified by a (here slightly modified) toy model of a possible explicit form by Perdew and Wang: If

$$a_x(K, \bar{k}_{\mathrm{Y}}) = \left(\frac{7}{81} + \frac{3}{81}\frac{K^2}{K^2 + \bar{k}_{\mathrm{Y}}^2}\right), \tag{5.16}$$

one finds that

$$\lim_{\bar{k}_{\mathrm{Y}} \to 0} \lim_{K \to 0} a_x(K, \bar{k}_{\mathrm{Y}}) = \frac{7}{81} \quad \text{(Sham result)}, \tag{5.17}$$

$$\lim_{K \to 0} \lim_{\bar{k}_{\mathrm{Y}} \to 0} a_x(K, \bar{k}_{\mathrm{Y}}) = \frac{10}{81} \quad \text{(Antoniewicz–Kleinman result)}. \tag{5.18}$$

The plots of Kleinman and Lee[56] indicate that the qualitative behavior of this example 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 on whether the gradient coefficient one should use may depend on how the correlation energy term is obtained—i.e., perhaps the errors in the Sham exchange are cancelled by errors in the Ma–Brueckner correlation. In 1989 Kleinman and Tamura[66] pointed out several problems with the work of Ma and Brueckner. Among other things they state: "*Thus the* $e^2$ *dependence of [the Ma–Brueckner correlation GEA coefficient] may be nothing more than a mathematical curiosity, valid only when the [density gradient], for which it is the coefficient, is identically zero.*" This casts some doubts on the accepted exchange and correlation coefficients of the GEA, and it is unknown to the present author if this has yet been fully resolved.

In a truly slowly varying system, GEA should improve on LDA, 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, discussed in the next few sections, has given very useful functionals.

## 5.5 Generalized-Gradient Approximations, GGAs

A *generalized-gradient approximation* (GGA) is abstractly defined as any generic function of the local value of the density and its squared gradient $s^2$ that is constructed to approximate the exchange-correlation energy per particle. Hence,

$$E_{xc}^{\mathrm{GGA}} = \int n(\mathbf{r})\epsilon_{xc}^{\mathrm{GGA}}(n(\mathbf{r}), s^2)d\mathbf{r}. \tag{5.19}$$

A GGA is thus not just meant to be a terminated power expansion valid only for low density gradients $s$, like GEA, but rather some expression that aims to give a generally applicable good approximation of the exchange-correlation energy per particle for all values of $s$.

The GGA's view of the density is solely through the local value of the density $n(\mathbf{r})$ and the density gradient $s$. It should be evident that there may be situations when this limited view does not discriminate between physically different situations. For example, certain points in the inter-shell regions of an atom look the same as points where the electron density decays exponentially (see section 7.3 and paper 2 of part III). In such cases, the GGA must use some kind of 'averaged' interpretation of what the values of $n(\mathbf{r})$ and $s$ mean. It follows that users who aim for different applications will prefer different GGAs 'tailored' to interpret the values in a context relevant for them. Hence, a wealth of different GGA expressions exist and there is an ongoing discussion on what makes the 'best and most general' GGA. The author has also contributed to this field by the derivation of a new functional on GGA form (presented in chapter 7 and paper 4 of part III).

The view of 'a GGA' as any expression on the form of Eq. (5.19) is in common use in literature. However, the term was first introduced in the context of the real-space cutoff procedure described in next section, so it is not uncommon to find presentations where the term is used in that more specific sense.

## 5.6 GGAs from the Real-space Cutoff Procedure

In a series of articles Perdew and coworkers have developed and refined a process of functional development known as the *real-space cutoff* technique (see Refs. 67–71 and references therein). For electronic densities which are not slowly varying, the GEA is not well behaved; in particular it violates the sum rule and the non-positivity constraint for exchange, Eqs. (4.15) and (4.26). The real-space cutoff solution[67,71] is to introduce a cutoff radius and use step functions in real-space to cut off the exchange hole at some $\mathbf{r}$. The step functions are chosen to force the expression to satisfy the sum rule as well as the non-positivity constraint. One argument for this procedure is that the description of the exchange-correlation hole by GEA is most accurate close to the electron but gets worse further away[70,72–75].

The derivation of Perdew, Burke and Wang from 1996 (Ref. 71) gives a clear account of the method. The GEA exchange hole is written as

$$n_x^{\mathrm{GEA}}(\mathbf{r}, \mathbf{r}+\mathbf{R}) = -\frac{1}{2}n(\mathbf{r})y(\mathbf{R}), \tag{5.20}$$

where the radial behavior of the exchange hole $y(\mathbf{R})$ is some known, but complicated, function. Two step functions[†] $\theta(x)$ are inserted to remove the properties of the hole that is the source of complications. The result is the exchange hole of the cutoff GGA,

$$n_x^{\mathrm{GGA}}(\mathbf{r}, \mathbf{r}+\mathbf{R}) = -\frac{1}{2}n(\mathbf{r})y(\mathbf{R})\theta(y(\mathbf{R}))\theta(R_c(\mathbf{r}) - |\mathbf{R}|). \tag{5.21}$$

The first step-function enforces the non-positivity constraint Eq. (4.26). The second uses a cutoff radius $R_c$ chosen to make the expression satisfy the sum rule Eq. (4.25). A similar technique is employed for the correlation hole: In the expression for the spherical averaged correlation hole, a step function is appended with a similar radial cutoff chosen to make it satisfy the correlation sum rule Eq. (4.30).

When the GEA hole is integrated with these cutoffs in place, one gets a *numerical GGA* that can be parameterized by an analytical expression. The result is a functional that can be applied in calculations.

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[†] The step function is defined as: $\theta(x) = 0$ for $x < 0$; and $\theta(x) = 1$ for $x \geq 0$.

## 5.7 Constraint-based GGAs

The GGA functional of Perdew and Wang 1991 (PW91; Refs. 69,70) uses the real-space cutoff scheme presented above but also chooses a form which ensures that some exact conditions are fulfilled. This approach was taken further by Perdew, Burke and Ernzerhof (PBE) in 1996 (Ref. 76) as they presented an alternative way of deriving a GGA functional. They derived all the coefficients from exact constraints and used no fitting to real-space cutoff data at all. The resulting GGA functional has been argued to be very similar to the one of Perdew and Wang. The similarity has been put forward as an argument for the generality of these GGAs. Paper 5 of part III raises some issues with this argued universal similarity.

The uniform gas is a well studied limiting case and therefore provides some of the most precise constraints used for creating constraint-based GGAs. However, there have been some arguments about whether imposing a correct uniform gas limit really is relevant for functionals used in e.g. quantum chemistry (see for example Becke's admitted wavering on the issue[77–79]). One other constraint has also been debated, the *Lieb–Oxford lower bound* [80],

$$E_x \geq -1.679 \left(\frac{e_c^2}{4\pi\epsilon_0}\right) \int n^{4/3}(\mathbf{r}) d\mathbf{r}. \tag{5.22}$$

In for example PBE this bound is implemented on a local level. Such an implementation is a more strict requirement that the regular Lieb–Oxford bound and may be unnecessarily strict (i.e., it might not be fulfilled by the exact functional). The *local Lieb–Oxford lower bound* is given by

$$\epsilon_x \leq 2.273\, \hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r})). \tag{5.23}$$

## 5.8 Meta-GGAs

To continue the approach of constructing expressions that fulfill more and more exact constraints, one has to introduce more information about the electron density than is given by the local values of the electronic density and its gradient $s$. This leads to the so called *meta-GGAs*. The logical extension of the GGA form would be to add further derivatives of the electron density, the Laplacian $q$ etc. However, functionals that include these parameters have been seen to be subject to great numerical difficulties when employed in a self-consistent Kohn–Sham scheme[81,82]. As an alternative, it is common to instead introduce the non-interacting kinetic energy density (see section 8.4),

$$\tau(\mathbf{r}) = \left(\frac{\hbar^2}{2m_e}\right) \sum_i |\nabla\phi_i(\mathbf{r})|^2, \tag{5.24}$$

with the sum taken over all occupied Kohn–Sham orbitals. An approximation of the exchange-correlation energy per particle that is dependent on the kinetic energy density is strictly not a density functional, but rather a local functional of the Kohn–Sham orbitals.

Along the lines of the general definition of a GGA, Eq. (5.19), one commonly use an abstract definition of a meta-GGA as a function of the local value of the density, its squared gradient $s^2$, its Laplacian $q$, and the kinetic energy density that is constructed to approximate the exchange-correlation energy per particle (but possibly one may also allow for other semi-local parameters). Hence,

$$E_{xc}^{\mathrm{mGGA}} = \int n(\mathbf{r})\epsilon_{xc}^{\mathrm{mGGA}}(n(\mathbf{r}), s^2, q, \tau)d\mathbf{r}. \tag{5.25}$$

## 5.9 Empirical Functionals

An alternative to the real-space cutoff scheme and/or satisfaction of exact constraint is the more pragmatic approach of *empirical functionals*. One of the earliest examples of an empirical functional is the *X*$\alpha$ *approximation* of Slater[83]. Among others, Becke and coworkers[84–86] have had a key role in the development of the empirical approach. Data are first produced for real systems, usually atomic or molecular. Useful data come from e.g. computer calculations for simple systems using very time-consuming methods that are more accurate than DFT, and from experiments. In any case, accurate data must somehow be produced *outside of DFT*. The data are then parameterized in the density $n(\mathbf{r})$, its derivatives (e.g., $s$ and $q$), and possibly other available parameters (e.g., $\tau$).

The empirical approach is commonly criticized for the risk that the functionals are too strongly influenced by the systems used for fitting. The resulting functionals may be very accurate for some classes of systems, but lack general applicability.

## 5.10 Hybrid Functionals

The idea of *hybrid functionals* grew out of the attempts to use DFT functionals as a computationally cheap way of correcting Hartree–Fock calculations for correlation effects. Becke formalized the approach[33] in an early hybrid theory that is interesting in itself. Start from the adiabatic connection formula Eq. (4.10) derived in section 4.2,

$$E_{xc} = \int_0^1 U_{xc}^{\lambda} d\lambda. \tag{5.26}$$

This integral can be approximated using the mean-value theorem of integration as

$$E_{xc} \approx \frac{1}{2}(U_{xc}^0 + U_{xc}^1) = \frac{1}{2}(E_x + U_{xc}^1), \tag{5.27}$$

where, in the last step, Becke argues[33] that $U_{xc}^0$ just is $E_x$ as defined in Eq. (4.22). The quantity $U_{xc}^1$ is the exchange-correlation potential energy of the fully interacting real system. An approximation for the latter can be constructed the same way LDA was constructed,

$$U_{xc}^1 \approx U_{xc}^{\mathrm{LDA}} = \int u_{xc}(n(\mathbf{r}))d\mathbf{r}. \tag{5.28}$$

The LDA-like functional $u_{xc}(n(\mathbf{r}))$ is derived as an LDA approximation of the potential energy part of the exchange-correlation energy, i.e., $U[n] - J[n]$, cf. Eq. (4.1). Becke obtains[33] an expression to use for $u_{xc}$ from the parameterization of regular LDA correlation by Perdew and Wang[45]. It was later shown[87] how an approximation of $U^1_{xc}$ can be created from any exchange-correlation functional. For a generic density functional approximation (DFA) one finds

$$U^1_{xc} \approx U^{\mathrm{DFA}}_{xc} = 2E^{\mathrm{DFA}}_{xc}[n] - \left.\frac{\partial E^{\mathrm{DFA}}_{xc}[n_\gamma]}{\partial \gamma}\right|_{\gamma=1}, \tag{5.29}$$

where $n_\gamma$ is the scaled density as defined in Eq. (4.27).

Becke's hybrid theory can be viewed both as an correlation correction to the Hartree–Fock scheme, and as a method for incorporating exact exchange into DFT calculations. Becke called it "*a true hybrid of its components*" and named the two-point adiabatic integration "*half-and-half theory*".

The half-and-half theory was followed by another *three-parameter hybrid formula* of Becke[88] that arguably is less connected to formal theory, but was more successful and constitutes the basis for several hybrid functionals in use (e.g., B3LYP[89,90]),

$$E_{xc} = a_0(E_x - E^{\mathrm{LDA}}_x) + E^{\mathrm{LDA}}_{xc} + a_x(E^{\mathrm{GGA}}_x - E^{\mathrm{LDA}}_x) + a_c(E^{\mathrm{GGA}}_c - E^{\mathrm{LDA}}_c). \tag{5.30}$$

Here $a_0$, $a_x$, and $a_c$ are empirical parameters. The use of scaling parameters in the last two terms, which represent the GGA's correction of LDA, was motivated by Becke with the argument that a GGA partly includes a correction of the failure of LDA to produce exact exchange in the $\lambda = 0$ limit. Since the formula manually corrects this problem the GGA's corrections must be scaled down.

However, it was remarked by Levy *et. Al.*[87], that the tree-parameter hybrid formula seems to be a step away from the formal adiabatic connection approach since it apparently drops the $\lambda$-derivative in Eq. (5.29). The empirical parameters may be able to correct for this fallacy. Furthermore, Perdew, Ernzerhof and Burke[91] looked at the formula with $a_x = a_c = 1$ and discussed its motivation starting from a simple model for the hybrid coupling-constant dependence:

$$U^\lambda_{xc} = E^{\mathrm{DFA}}_{xc,\lambda} + (E_x - E^{\mathrm{DFA}}_x)(1-\lambda)^{k-1}, \tag{5.31}$$

with $k$ an unknown integer. They found that this model led to a theoretical motivation for choosing the value $a_0 \approx 0.25$.

To implement hybrid functionals in computer code it is quite common to use Hartree–Fock exchange to approximate the exact Kohn–Sham exchange used in the derivation of the Hybrid theory. It is possible that this approximation is somewhat compensated for in the fit of empirical parameters.

## Chapter 6

# A Gallery of Functionals

*What is your substance, whereof are you made,*
*That millions of strange shadows on you tend?*
William Shakespeare

The previous chapter presented a number of general techniques for the development of exchange-correlation functionals. In this chapter we go through the most commonly known functionals developed with these techniques.

## 6.1 The GGA of Perdew and Wang (PW91)

The GGA of Perdew and Wang[69,70] from 1991 (PW91) is a nonempirical functional based on fitting to a numerical GGA produced by the real-space cutoff procedure described in section 5.6. When the dimensionless gradient $s \to 0$, i.e. in the limit of slowly varying and high density limits, the PW91 parameterization is chosen to reproduce a second-order GEA, Eq. (5.11), with Shams $a_x$ and the $A_c(n(\mathbf{r}))$ of Rasolt and Geldart (cf. section 5.4). PW91 improves on LDA for most chemical systems, and for certain properties of materials. For systems with electronic surfaces, such as vacancy systems, PW91 is inferior to LDA [92]. PW91 does not describe the correct uniform scaling to the high density limit. It often gives spurious wiggles in the exchange-correlation potential for small and large $s$.

## 6.2 The GGA of Perdew, Burke, and Ernzerhof (PBE)

The GGA of Perdew, Burke, and Ernzerhof[76] from 1996 (PBE) is a nonempirical functional with parameters derived to satisfy a specific set of exact constraints. This approach was discussed in section 5.8. PBE does not reproduce a second-order GEA for slowly varying densities. Instead it provides a better description of the linear response limit[†]. PBE reduces to the LDA for slowly varying densities. It does not uphold a scaling limit that PW91 upholds (the nonuniform scaling of $E_x$ in limits where the reduced gradient $s \to \infty$). The PBE authors argue that this constraint is energetically unimportant.

The PBE functional turns out to be very similar to PW91. In fact, PBE and PW91 are often argued to be roughly equivalent for applications; but paper 5 in part III raises some issues with the similarity between the functionals. As for PW91, PBE's results for vacancy formation energies are inferior to LDA (see papers 4 and 5 of part III). PBE does not have the spurious wiggles in the exchange-correlation potential found for PW91, and therefore is more suitable for e.g. pseudopotentials.

## 6.3 Revisions of PBE (revPBE, RPBE)

Zhang and Yang[93] remarked that enforcing the local Lieb–Oxford bound in the construction of the PBE exchange functional may be too strict. They proceeded by constructing a functional revPBE that entirely ignored the bound and instead turned one of the PBE parameters into an empirical value by fitting it to total atomic energies from helium to argon. They argued that since revPBE still fulfilled the *regular* Lieb–Oxford bound for all their test systems (atoms and molecules), this could be a general feature of the functional. The work presented data of improved atomization energies for small molecules. Furthermore, Hammer, Hansen, and Nørskov found that revPBE also improved upon PBE for chemisorption energetics of atoms and molecules on transition-metal surfaces[94]. They also presented a further revised revPBE functional (RPBE) that reintroduced the local Lieb–Oxford bound.

However, it has been seen that RPBE and revPBE do not always improve on PBE [95]. For example, some material properties are in larger disagreement with experimental results compared to PBE. This leads us back to one of the points of section 5.5; the way a GGA interprets the information it is given can be more or less tailored towards certain applications.

## 6.4 The Exchange Functionals of Becke (B86, B88)

Becke presented an empirical exchange functional in 1986 (B86). It proposes an analytical form based on the GEA, but damps the $s$-dependence to avoid the problems related to the divergent behavior of the GEA. It contains two empirical parameters determined by fitting to Hartree–Fock exchange energies of 20 atomic systems. Various improvements to the analytical form were later presented by Becke and other authors. The exchange functional of PBE is in fact based on the B86 expression, but determines the parameters non-empirically.

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[†] The *linear response limit* means wiggles of small amplitude on a uniform electron gas; the GGA form is too restricted to simultaneously get both this limit right and reproduce a specified second-order GEA.

In 1988 Becke presented an improved exchange functional (B88) that has become popular, in particular for applications in quantum chemistry. The goal was to reproduce a correct asymptotic behavior for the exchange energy per particle outside a finite system. It leaves one parameter to be determined empirically. Becke fitted its value using Hartree–Fock exchange energies of six noble-gas atoms.

## 6.5 The Correlation Functional of Lee, Yang, and Parr (LYP)

Colle and Salvetti[96] presented a formula for the correlation energy in 1975. The formula was essentially based on a theoretical analysis that started from the Hartree–Fock second-order density matrix rescaled with a correlation factor. Four empirical parameters were determined by a fit to exact data for the helium atom. The formula was found to give good correlation energies for atoms and molecules. Lee, Yang and Parr reworked the Colle–Salvetti formula into a density functional (LYP). The LYP functional has been used very successfully in quantum chemistry together with the B88 functional (BLYP), in particular in the hybrid scheme called B3LYP[89,90]. BLYP and B3LYP are among the most popular functionals for quantum chemistry, but they perform badly for more electron-gas like applications, like e.g. solid-state systems[95].

One of the major criticisms raised against LYP is that it does not reproduce LDA in the limit of slowly varying densities. It therefore is not surprising that it performs badly for more electron-gas like systems, e.g. solids[95]. Another issue is that LYP becomes zero for a fully spin-polarized system, which is not correct for a multi-electron system.

## 6.6 The Meta-GGA of Perdew, Kurth, Zupan, and Blaha (PKZB)

Perdew, Kurth, Zupan, and Blaha[97] presented in 1999 a meta-GGA (PKZB) that built on PBE but added one more input parameter to the GGA form, the kinetic energy density. PKZB thus is a meta-GGA as discussed in section 5.8. The extra parameter makes it possible to satisfy more exact constraints. Among other features, the PKZB functional reproduces both a fourth-order GEA, and a specified linear response function up to forth order in the wave-vector. The correlation part of PKZB is based on a self-correlation correction to PBE's correlation. The PKZB functional contains one empirical parameter determined by fitting to atomization energies of 20 small molecules (The magnitude of this parameter was also argued from surface exchange energies of slowly varying densities.)

PKZB improves on PBE for several applications, e.g., surface and atomization energies[95,97,98]. However, it also gives poor equilibrium bond lengths and hydrogen-bonded complexes[98,99].

## 6.7 The Meta-GGA of Tao, Perdew, Staroverov, and Scuseria (TPSS)

Tao, Perdew, Staroverov, and Scuseria presented an improved meta-GGA[100,101] (TPSS) in 2003. Similar to PKZB, TPSS adds the kinetic energy density as a parameter to the GGA form. The construction of TPSS starts from PKZB and, among other improvements, eliminates the need for an empirical parameter. Extensive tests have been performed[100,102,103], and the TPSS authors conclude that the tests indicate a general, but moderate, improvement of PBE[102].

## Part II

# SCIENTIFIC CONTRIBUTION

## Chapter 7

# SUBSYSTEM FUNCTIONALS

> *Great acts are made up of small deeds.*
>
> Lao Tsu

This chapter presents the subsystem functional approach to functional development. More details on the material discussed here are given in paper 1 of part III.

## 7.1 General Idea

The subsystem functional approach is based on the idea of locality (near-sightedness) of the electron gas[4,5]. The *near-sightedness* is explained as the observation that an electron is mainly influenced by those other electrons that are closest. Thus, the electron's behavior should be governed by local or semi-local properties of the electron gas.

We start from the implicit definition of the exchange-correlation energy per particle Eq. (4.2),

$$E_{xc} = \int n(\mathbf{r})\epsilon_{xc}(\mathbf{r})d\mathbf{r}. \tag{7.1}$$

This integration over all space may be decomposed into integrations over several separate spatial regions $R_1$, $R_2$, ...;

$$E_{xc} = \int_{R_1} n(\mathbf{r})\epsilon_{xc}(\mathbf{r})d\mathbf{r} + \int_{R_2} n(\mathbf{r})\epsilon_{xc}(\mathbf{r})d\mathbf{r} + ... + \int_{R_N} n(\mathbf{r})\epsilon_{xc}(\mathbf{r})d\mathbf{r}. \tag{7.2}$$

This general idea was illustrated in chapter 1 in Fig. 1.4.

Approximations to $\epsilon_{xc}$ that can be applied in a partial system like in Eq. (7.2) are *subsystem functionals*. Obviously, a subsystem functional may not be based on the assumption that it will be used in the whole system. Rather, it must give a valid approximation of the integrated value of some exact $\epsilon_{xc}$ when integrated over only a part of a system. We have previously discussed that the implicit definition of $\epsilon_{xc}$ leaves a freedom of choice. All integrations over parts in Eq. (7.2) must approximate integrated values of one and the same choice of $\epsilon_{xc}$. This is required for the contributions from the different parts to sum up to the correct total exchange-correlation energy. The straightforward way to enforce this is if all subsystem functionals applied to a system are taken to approximate the conventional exchange-correlation energy per particle $\hat{\epsilon}_{xc}$. Paper 1 of part III discusses this in some more detail.

The reason why the above discussion is about a partition in real space, as opposed to $k$-space, is the view of a near-sighted electron gas. One could create a partition in $k$-space by performing a Fourier-transform of Eq. (7.1) and then partitioning the integral, but this approach has not been formally investigated. To further pursue the idea one needs to make a careful examination of what concept of locality is used and discuss for what kinds of systems the $k$-space approach would be useful.

The subsystem functional scheme has similarities to the *divide and conquer* scheme of Yang[104,105], but the two approaches are not identical. The latter divides the entire Kohn–Sham iteration to be over separate subregions. The subsystem functional scheme leaves the Kohn–Sham scheme unmodified, and the subdivision of a system only occurs within the exchange-correlation functional.

## 7.2 Designing Functionals

The functionals presented in chapter 6 use different, unknown, choices of the exchange-correlation energy per particle. For example, they are derived using GEA power series integrated by parts and empirical coefficients. While they approximate the correct total exchange-correlation energy when integrated, their specific local values of $\epsilon_{xc}$ *cannot* be seen as an approximation to the local conventional choice $\hat{\epsilon}_{xc}$. The lack of a consistent choice of $\hat{\epsilon}_{xc}$ in different functionals means that they cannot be combined into a subsystem functional scheme. Basically, the functionals have been derived on the assumption that they will be used throughout the space of integration.

To discuss the development of functionals that work in a subsystem functional setting we have to start from the local density approximation, which approximates the conventional exchange-correlation energy per particle $\hat{\epsilon}_{xc}$. Much of papers 1 and 3 of part III deal with how to go beyond LDA in the form of a GEA of a local exchange energy per particle and turn it into a functional for slowly varying electron densities. A local GEA is derived in paper 3, where also a redistribution of exchange and correlation is performed; a requirement for the GEA to exist (see section 9.2).

To create subsystem functionals for systems where the electron density is not slowly varying one can use model systems. The exchange functional for electronic surfaces that is designed in paper 4 is one example of such use of model systems. The functional is based on a model where the effective potential is linear. It will be discussed more in section 7.4 and forward.

## 7.3 Density Indices

We will now discuss the non-trivial problem of performing the partitioning of a system into subsystems. One approach is to have a computational scientist manually part the system into subregions. In this case the partitioning would be based on the physical insight of the system that the scientist has.

A more automatic approach is to build into the functional a mechanism for deducing how to partition the system. An automatic separation into parts can be created using one or more density indices. A *density index* is a functional of the electron density, which for each space point gives a value between 0 or 1 that describes to what extent the density in this point can be said to be of a specific type. For example, an index can tell whether the density in a space point is on an 'electronic surface' as opposed to e.g. in the interior of a system. Another example would be to determine to what extent points of the density are atom-like.

Let one subsystem functional be the generic functional that is to be used where no other model is suitable, $\hat{\epsilon}_{xc}^{(0)}$. This generic functional can, for example, be ordinary LDA. Then imagine a series of subsystem functionals based on different models $\hat{\epsilon}_{xc}^{(1)}$, $\hat{\epsilon}_{xc}^{(2)}$ ... $\hat{\epsilon}_{xc}^{(N)}$. For each of these functionals one has an index, $I^{(1)}$, $I^{(2)}$, ..., $I^{(N)}$. A straightforward way to construct an interpolating subsystem functional (ISF) is,

$$\hat{\epsilon}_{xc}^{\mathrm{ISF}} = X\hat{\epsilon}_{xc}^{(0)} + \sum_{n=1}^{N} \frac{I^{(n)}}{N} \hat{\epsilon}_{xc}^{(n)}, \tag{7.3}$$

where

$$X = \left(1 - \sum_{n=1}^{N} \frac{I^{(n)}}{N}\right). \tag{7.4}$$

However, for functionals that are based on an asymptotic behavior one has to be careful. The indices must be designed to interpolate in a way that preserves the correct limiting behavior.

Paper 2 in part III deals with the construction of a density index that describes how atom-like the density is. It is seen how an elaborate construction involving electron density and kinetic energy density derivatives is needed to get all parts of the intershell regions of an atom correctly classified. However, we note that for an actual DFT calculation it may not be absolutely necessary to use an index with this precision. Even if the density is interpreted incorrectly in 'a few points' in the intershell regions, it may be sufficient to be right in the major part of the system to reach good accuracy. Furthermore, the index constructed in paper 2 classifies a point of the density using only information available in that specific spatial point, i.e., electron density and kinetic energy values and derivatives. An index that uses more than just the local information might reach the same precision without elaborate kinetic energy derivatives.

## 7.4 A Straightforward First Subsystem Functional

We will now demonstrate the subsystem functional scheme by the construction of a 'first' simple subsystem functional. The approach is the one of paper 4 in part III (which in the following is referred to as AM05), but some additional details are given.

The construction starts from the interpolation formula presented in the previous section. Ordinary LDA is used for the base functional $\hat{\epsilon}_{xc}^{(0)}$. One other functional is used along with LDA, a functional to specifically treat electronic surfaces. An electronic surface is a region where the electron density rapidly decreases, e.g., outside a surface system or inside a vacancy. Roughly, one can think of electronic surfaces in terms of the classical turning points of a system's most energetic electrons.

When only two functionals are involved in a subsystem functional scheme, the interpolation formula Eq. (7.3) reduces to

$$\hat{\epsilon}_{xc}^{\text{DFA}} = X\hat{\epsilon}_{xc}^{\text{LDA}} + (1-X)\hat{\epsilon}_{xc}^{\text{surf}}. \tag{7.5}$$

To complete this functional we thus need an interpolation index $X$ and an exchange-correlation functional for surface systems $\epsilon_{xc}^{\text{surf}}$. These components will be addressed in the following.

## 7.5 A Simple Density Index for Surfaces

The dimensionless gradient $s$ diverges outside an electronic surface. The reason is that the electron density $n$ appears in the denominator of the definition of $s$, Eq. (5.8), and in this limit $n \to 0$. An index $I$ that increases towards 1 the more 'surface like' the electron density is can thus be created as

$$I = \frac{\alpha s^2}{1+\alpha s^2}. \tag{7.6}$$

In the interpolation formula Eq. (7.5) we then use $X = (1-I)$. The scalar parameter $\alpha$ is a *surface position parameter*. When the index interprets the electron density, this parameter adjusts the overall inward-outward position of the electronic surface. To use the index one has to provide the parameter $\alpha$ or determine it in some way. Below we will use a fitting procedure to obtain a useful value of $\alpha$.

## 7.6 An Exchange Functional for Surfaces

In AM05 an exchange functional is constructed to target surface regions of the electron density. One starts from the *Airy gas* model system[5]. The Airy gas is a model of Kohn–Sham particles in a linear potential, $v_{\text{eff}}(\mathbf{r}) = Lz$. It models an electronic surface where the classical turning point of the most energetic Kohn–Sham particles is at $z = 0$. The parameter $L$ sets an overall length scale. It is used to rescale the exchange energy per particle $\hat{\epsilon}_x$ and the density $n(\mathbf{r})$ into dimensionless and scale-independent quantities; $\hat{\epsilon}_{x,0}^{\text{Airy}} = L^{-1/3}\hat{\epsilon}_x(\mathbf{r};[n])$, and $n_0 = L^{-1}n(\mathbf{r})$. By solving the Kohn–Sham orbital equation

Eq. (3.11), and then inserting the orbitals in the usual expressions for the exchange energy Eqs. (4.23)–(4.24) and electron density Eq. (2.14), one arrives at[5]

$$\begin{aligned}\hat{\epsilon}_{x,0}^{\text{Airy}} = \frac{-1}{\pi n_0}\int_{-\infty}^{\infty} d\zeta' \int_0^{\infty} d\chi \int_0^{\infty} d\chi' \, \frac{g(\sqrt{\chi}\Delta\zeta, \sqrt{\chi'}\Delta\zeta)}{\Delta\zeta^3} \\ \times \text{Ai}(\zeta+\chi)\text{Ai}(\zeta'+\chi)\text{Ai}(\zeta+\chi')\text{Ai}(\zeta'+\chi'),\end{aligned} \tag{7.7}$$

where $\zeta = L^{1/3}z, \;\; \Delta\zeta = |\zeta - \zeta'|$, and

$$g(\eta, \eta') = \eta\eta' \int_0^{\infty} \frac{J_1(\eta t)J_1(\eta' t)}{t\sqrt{1+t^2}} dt. \tag{7.8}$$

In AM05 the density is given on explicit form

$$n_0 = \frac{1}{3\pi}\left(\zeta^2 \text{Ai}^2(\zeta) - \zeta \text{Ai}'^2(\zeta) - \frac{\text{Ai}(\zeta)\text{Ai}'(\zeta)}{2}\right). \tag{7.9}$$

Taking derivatives of the density expression directly gives

$$s = \frac{1}{2(3\pi^2)^{1/3} n_0^{4/3}}\left|\frac{dn_0}{d\zeta}\right|, \quad \frac{dn_0}{d\zeta} = \frac{\zeta \text{Ai}^2(\zeta) - \text{Ai}'^2(\zeta)}{2\pi}, \tag{7.10}$$

$$q = \frac{1}{4(3\pi^2)^{2/3} n_0^{5/3}}\frac{d^2 n_0}{d\zeta^2}, \quad \frac{d^2 n_0}{d\zeta^2} = \frac{\text{Ai}^2(\zeta)}{2\pi}. \tag{7.11}$$

A functional based on the Airy gas model should relate a real system's electron density in a given spatial point to that of an Airy gas for which the density behavior semi-locally is as similar to the real system as possible. There is more than one possible implementation of this. The most straightforward approach is to take the exchange energy from an Airy gas model that has the same local value of the electron density $n$ and density gradient $\nabla n$ as the real system. The approach has similarities to the construction of LDA in section 5.2. AM05 presents a parameterization of the Airy gas exchange energy: the Local Airy Approximation (LAA). In the following we give some details of the construction of the parameterization that is not given in AM05.

The real system's local value of the electron density in a given spatial point is automatically reproduced by the Airy gas model if the right length scale is chosen; $L = n/n_0$. The Airy exchange energy $\hat{\epsilon}_x^{\text{Airy}}$ thus can be separated into a prefactor $n^{1/3}$ and a dimensionless and density-scale invariant function. This separation is just a special case of the general separation of the exchange energy per particle into LDA and a refinement factor, as previously discussed in section 5.3. The dimensionless Airy refinement factor $F_x^{\text{Airy}}(s)$ is a function of the dimensionless gradient $s$ and is defined by

$$\hat{\epsilon}_x^{\text{Airy}}(\mathbf{r};[n]) = \hat{\epsilon}_x^{\text{LDA}}(n(\mathbf{r}))F_x^{\text{Airy}}(s). \tag{7.12}$$

It can be expressed in the rescaled dimensionless Airy quantities as

$$F_x^{\text{Airy}}(s) = \frac{L^{1/3}\hat{\epsilon}_{x,0}^{\text{Airy}}}{\hat{\epsilon}_x^{\text{LDA}}(n(\mathbf{r}))} = \frac{\hat{\epsilon}_{x,0}^{\text{Airy}}}{\hat{\epsilon}_x^{\text{LDA}}(n_0)}. \tag{7.13}$$

A parameterization of $F_x^{\mathrm{Airy}}(s)$ is needed to use the Airy gas in density functional theory computations. One such parameterization is already available, the *Local Airy Gas* [106]:

$$F_x^{\mathrm{LAG}}(s) = 1 + a_\beta s^{a_\alpha}/(1 + a_\gamma s^{a_\alpha})^{a_\delta}, \tag{7.14}$$

$$a_\alpha = 2.626712,\ a_\beta = 0.041106,\ a_\gamma = 0.092070,\ a_\delta = 0.657946. \tag{7.15}$$

However, the subsystem functional we are constructing needs a high-accuracy expression for use in electronic surface regions. The LAG parameterization was constructed as a universally acceptable expression for all parts of a system. It is not safe to assume that this parameterization is accurate enough for our purposes, i.e., especially in the region far outside the surface. Because of this, an improved parameterization is derived.

The derivation starts with the asymptotic behavior far outside the surface, which is the key difference between the Airy parameterization constructed here and the one already available (LAG). The paper of Kohn and Mattsson on the Airy gas[5] gave the asymptotic behavior of the Airy gas exchange energy per particle as $\hat{\epsilon}_{x,0}^{\mathrm{Airy}} \to -1/(2\zeta)$. The quantity $\zeta$ can be transformed into an expression in $s$ by inserting asymptotic expressions for the Airy functions into Eq. (7.10) (carefully including a sufficient number of terms) and inverting. The procedure results in a function $\tilde{\zeta}(s)$ that approaches the regular $\zeta$ in the $s \to \infty$ limit,

$$\tilde{\zeta}(s) = \left[\frac{3}{2} W\left(\frac{s^{3/2}}{2\sqrt{6}}\right)\right]^{2/3}, \quad \epsilon_{x,0}^{\mathrm{Airy}} \to -\frac{1}{2\tilde{\zeta}}, \tag{7.16}$$

where $W(x)$ is the Lambert $W$-function[107]; the solution $w$ to $x = we^w$. To describe the asymptotic behavior of $F_x^{\mathrm{Airy}}(s)$, the LDA factor $\hat{\epsilon}_x^{\mathrm{LDA}}(n_0)$ must also be expressed as a function of $s$ that is correct in the $s \to \infty$ limit. An expression for this LDA factor is given by inserting asymptotic expansions of the Airy functions in Eq. (7.9) and then let $\zeta \to \tilde{\zeta}(s)$. The result is

$$\tilde{n}_0(s) = \frac{\tilde{\zeta}(s)^{3/2}}{3\pi^2 s^3}, \quad F_x^{\mathrm{Airy}}(s) \to -\frac{1}{\hat{\epsilon}_x^{\mathrm{LDA}}(\tilde{n}_0(s))2\tilde{\zeta}(s)}. \tag{7.17}$$

This expression for $F_x^{\mathrm{Airy}}(s)$ is formally valid in the $s \to \infty$ limit, but it is observed to be fairly useful even for finite $s$. To improve it for low $s$, it should be made to approach the LDA, i.e., one wants $F_x(s) \to 1$ in the $s \to 0$ limit. The actual behavior of the $s \to \infty$ asymptotic expression in the $s \to 0$ limit is found by expanding it around $s = 0$. The leading term is $\sqrt{2/3}\, 4\pi/(3s^{1/2})$. However, if one makes the change $\tilde{\zeta}(s) \to \tilde{\zeta}(s)^{1/2}$, then the leading term turns into a constant. Thus the asymptotic $s \to \infty$ and the LDA $s \to 0$ limits can be fulfilled simultaneously by creating a new "effective" interpolated $\zeta$-coordinate. The following definition of the effective coordinate does a good job in describing the transition,

$$\tilde{\tilde{\zeta}}(s) = \left(C^4\tilde{\zeta}(s)^2 + \tilde{\zeta}(s)^4\right)^{1/4}, \quad C = (4/3)^{1/3}2\pi/3. \tag{7.18}$$

The scalar $C$ is chosen to make $F_x(s)$ approach 1 (rather than some other constant value). The new interpolated refinement factor

$$F_x^b(s) = -\frac{1}{\hat{\epsilon}_x^{\mathrm{LDA}}(\tilde{n}_0(s))2\tilde{\tilde{\zeta}}(s)} \tag{7.19}$$

still deviates slightly from actual computed values for intermediate values of $s$. This can be improved if the expression is pushed slightly more towards LDA in a way difficult to accomplish by further adjusting Eq. (7.18). The last step therefore is to interpolate the above expression towards LDA (despite the fact that it already does approach LDA). The final expression becomes

$$F_x^{\mathrm{LAA}}(s) = (cs^2+1)/(cs^2/F_x^b(s)+1), \quad c = 0.7168, \tag{7.20}$$

where $c$ is obtained through a least-squares fit to the exact Airy exchange data obtained from Eq. (7.7). The LAA parameterization makes a small improvement to LAG in the region of intermediate $s$, but the improvement becomes significant for larger $s$ (i.e. outside the electronic surface; see Fig. 1 in AM05).

## 7.7 A Correlation Functional for Surfaces

The preferred way of creating a correlation functional that matches the Airy gas exchange functional would be to parameterize exact correlation energy per particle data for the Airy gas model. Such data should be possible to compute by e.g. Monte Carlo methods. However, no correlation data for the Airy gas are yet available to parameterize. Therefore the correlation functional that is matched with the Airy exchange functional in AM05 is created by a fitting procedure that instead involves jellium surface energies.

The *jellium surface model* is a model system with a uniform background of positive charge $\bar{n}$ for $z \leq 0$ and 0 for $z > 0$[108]. The value of $\bar{n}$ is commonly expressed in the dimensionless radius of the sphere that contains the charge of one electron $r_s$ as defined in Eq. (5.3). The *jellium surface energy* of a density functional approximation (DFA) $\epsilon_{xc}^{\mathrm{DFA}}(\mathbf{r};[n])$ is given by

$$\sigma_{xc}^{\mathrm{DFA}} = \int n(z)\left(\epsilon_{xc}^{\mathrm{DFA}}(\mathbf{r};[n]) - \hat{\epsilon}_{xc}^{\mathrm{LDA}}(\bar{n})\right) dz. \tag{7.21}$$

An LDA correlation adjusted with a multiplicative factor $\gamma$ is used for the surface correlation functional; $\hat{\epsilon}_c^{\mathrm{surf}} = \gamma\hat{\epsilon}_c^{\mathrm{LDA}}$. The multiplicative factor provides an adjustment of the LDA correlation energy that scales reasonable with the area of the electronic surface. It is believed that the most accurate jellium surface energies are given by the improved *random-phase approximation scheme* presented by Yan *et al.*[109] (RPA+). The RPA+ values are cited as integers in the unit $\mathrm{erg/cm}^2$, and therefore we assume that the absolute errors are roughly equal throughout all the values (meaning $\sigma_{xc}$ for smaller $r_s$ have smaller relative errors due to their greater magnitude). Hence, it is reasonable to let the least squares fit minimize an unweighted least squares sum $\sum_{r_s}|\sigma_{xc}^{\mathrm{AM05}} - \sigma_{xc}^{\mathrm{RPA+}}|^2$. The fit in AM05 uses the RPA+ values for $r_s = 2.0$, 2.07, 2.3, 2.66, 3.0, 3.28, and 4.0 to simultaneously fit the surface position $\alpha$ in Eq. (7.6) and the LDA correlation factor $\gamma$,

$$\alpha_{\mathrm{LAA}} = 2.804, \quad \gamma_{\mathrm{LAA}} = 0.8098. \tag{7.22}$$

This completes the functional,

$$\begin{aligned} \epsilon_x(\mathbf{r};[n]) &= X\hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r})) + (1-X)\hat{\epsilon}_x^{\mathrm{LDA}}(n)F_x^{\mathrm{LAA}}, \\ \epsilon_c(\mathbf{r};[n]) &= X\hat{\epsilon}_c^{\mathrm{LDA}}(n(\mathbf{r})) + (1-X)\gamma\hat{\epsilon}_c^{\mathrm{LDA}}(n). \end{aligned} \tag{7.23}$$

## 7.8 Outlook and Improvements

The simple functional constructed in the previous sections has been tested for a few solid state systems and performs well (see the test results in AM05 for details). Still, there are several future directions open for improving our currently rather crude procedure:

- One should develop a less rudimentary density index that does a better job in distinguishing between interior and surface regions.
- A better correlation functional for surfaces would most likely improve the results.
- LDA has been used for the interior region. A better approximation for near-uniform electron gas system, e.g. a gradient corrected functional, would probably improve the results further.
- Subsystem functionals for other types of systems can be derived and incorporated into the scheme. For example, a subsystem functional tailored for atomic intershell regions of the electron density may improve the exchange-correlation energy for such regions.

Naturally, the author hopes to see future development along one or more of these suggested improvements of the scheme.

Chapter 8

# THE MATHIEU GAS MODEL

> *What distinguishes a mathematical model from, say, a poem, a song, a portrait or any other kind of "model," is that the mathematical model is an image or picture of reality painted with logical symbols instead of with words, sounds or watercolors.*
>
> John Casti

Much of paper 1 in part III of this thesis deals with the numerical study of a specific model system, the Mathieu gas. This chapter introduces the model and discusses its usefulness as a DFT model system.

## 8.1 Definition of the Mathieu Gas Model

The *Mathieu gas* (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 system of Kohn–Sham particles moving in an effective potential

$$v_{\text{eff}}(\mathbf{r}) = \mu\bar{\lambda}(1 - \cos(2\bar{p}\bar{z})). \tag{8.1}$$

Here $\mu$ is the chemical potential of the system and $\bar{z} = k_{F,u}z = (2m\mu/\hbar^2)^{1/2}z$ is the $z$ coordinate scaled with the Fermi wave vector of a uniform electron gas. By solving the corresponding non-interacting electron system for specific values of $\bar{\lambda}$ and $\bar{p}$, the Kohn–Sham orbitals are obtained, and consequently gives an electron density.

## 8.2 Electron Density

Solving the MG effective potential system for the Kohn–Sham orbitals is significantly easier than it would be for a general system. As the effective potential only depends on the $z$

coordinate, the Kohn–Sham orbital equation can be separated into three one-dimensional equations. The Fermi surface of a one-dimensional system is only a point, which greatly simplifies the integration over occupied states. In a non-separable three-dimensional system, the treatment of the Fermi surface is not straightforward.

With constant $x$ and $y$ dimensions the Kohn–Sham orbitals take the form

$$\phi_\nu(x,y,z) = \frac{1}{\sqrt{L_1 L_2}} e^{i(k_1 x + k_2 y)}\, \varphi_\eta(z), \tag{8.2}$$

where $\nu$ specifies $k_1, k_2$ and $\eta$; $L_1 L_2$ is the $x, y$ area of the system and will approach infinity; $k_i L_i = 2\pi m_i$ ($i = 1, 2$, $m_i$ integer); and finally $\varphi_\eta(z)$ is the one-dimensional $z$-direction Kohn–Sham orbital. This orbital is determined by the following Kohn–Sham equation;

$$\left(-\frac{\hbar^2}{2m_e}\frac{d^2}{dz^2} + v_{\text{eff}}(z)\right)\varphi_\eta(z) = \epsilon_\eta \varphi_\eta(z). \tag{8.3}$$

Inserting the MG $v_{\text{eff}}$ gives the Mathieu differential equation, for which the solutions are known (see Ref. 110 for definitions of the Mathieu function symbols, $se_\eta$, $ce_\eta$, $a_\eta$ and $b_\eta$)

$$\varphi_\eta(z) = \begin{cases} (1/\sqrt{L})\, ce_\eta(\bar{p}\bar{z}, -\bar{\lambda}/(2\bar{p}^2)) \text{ if } \eta > 0 \\ (1/\sqrt{L})\, se_\eta(\bar{p}\bar{z}, -\bar{\lambda}/(2\bar{p}^2)) \text{ if } \eta < 0 \end{cases}, \tag{8.4}$$

$$\epsilon_\eta = \begin{cases} \mu(\bar{p}^2 a_\eta + \bar{\lambda}) \text{ if } \eta > 0 \\ \mu(\bar{p}^2 b_\eta + \bar{\lambda}) \text{ if } \eta < 0 \end{cases}, \tag{8.5}$$

$$n(\mathbf{r}) = \frac{k_{F,u}^3}{4\pi^2}\bar{p}\int_{-\tilde{\eta}}^{\tilde{\eta}} L|\varphi_\eta(z)|^2 \left(1 - \frac{\epsilon_\eta}{\mu}\right) d\eta, \tag{8.6}$$

where $\tilde{\eta}$ is the largest possible $\eta$ that fulfils $\epsilon_\eta \leq \mu$.

However, numerical calculations based on these formulas require computer routines for the Mathieu functions $ce$ and $se$. Such routines are produced by going back to the Mathieu differential equation, Eq. (8.3), and solve it by standard matrix methods. Once the Kohn–Sham orbitals are known, the conventional exchange energy per particle and other quantities can be obtained by direct numerical calculation. The data in Figs. 7–12 of paper 1 in part III were essentially produced by this method. Details on how to compute the Mathieu functions and how to perform the integrations above are presented in paper 1.

The energy expression of the MG model, Eq. (8.5), shows a rudimentary energy-band structure. The parameter $\eta$ indexes the band structure, much like the wave vector in an extended Brillouin zone-scheme.

## 8.3 Exploring the Parameter Space of the MG

The MG model spans a wide variety of systems over the range of possible $\bar{\lambda}$ and $\bar{p}$. We have found it useful to investigate some specific limits in the MG. These limits of the MG constitutes model systems on their own.

### 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. The data were therefore plotted versus a new parameter $\alpha$ that index the energy structure of the MG as a function of $\bar{\lambda}$ and $\bar{p}$;

$$\alpha = \frac{\mu - \epsilon_{\eta_1}}{\epsilon_{\eta_2} - \epsilon_{\eta_1}} + |\eta_1|, \tag{8.7}$$

where, if $\mu$ is inside a $z$-dimension energy band, $\epsilon_{\eta_1}$ is the lowest energy in this band. If $\mu$ is not inside an energy band, $\epsilon_{\eta_1}$ is the lowest energy in the band which contains the $z$-dimension energy state with highest energy $\leq \mu$. Furthermore, $\epsilon_{\eta_2}$ is the lowest possible energy of all $z$-dimension energy states within bands that only contain energies $> \mu$. By construction $\eta_1$ and $\eta_2$ are integer.

The parameter $\alpha$ 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 $\alpha$ differs from $\eta$ 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.

### The Free Electron Gas Limit

When $\bar{\lambda} \to 0$, the MG effective potential, Eq. (8.1), approaches a constant potential. This makes the solutions of the MG differential equation approach the plane wave solutions to a free electron (FE) gas,

$$\varphi_\eta(z) = \frac{1}{\sqrt{L_3}} \exp(i\eta\bar{p}\bar{z}), \tag{8.8}$$

$$\epsilon_\eta = \mu\eta^2\bar{p}^2. \tag{8.9}$$

Hence, in this limit the MG model describes a weakly perturbed uniform gas. For some finite but low $\bar{\lambda}$ a crystal-like system is described. This view was used in paper 2 to create a model of sodium and calcium crystals.

In the FE limit the $\alpha$ parameter reduces to

$$\alpha_{FE} = \frac{1/\bar{p}^2 + N(N+1)}{2N+1}, \quad N = \left\lfloor \frac{1}{\bar{p}} \right\rfloor. \tag{8.10}$$

### The Harmonic Oscillator Limit

In the limit $\bar{\lambda}/\bar{p}^2 \to \infty$ the MG effective potential approaches an harmonic oscillator (HO) potential. The energy structure in this limit becomes

$$\epsilon_n = \mu\sqrt{2\bar{\lambda}\bar{p}^2}\,(2n+1)\,. \tag{8.11}$$

The relation describes equally spaced energy levels (with spacing $\mu\sqrt{2\bar{\lambda}\bar{p}^2}$), much like a typical text book HO system. The corresponding Kohn–Sham orbitals are:

$$\begin{aligned}\varphi_n(z) = \left(\frac{k_{F,u}(\sqrt{2\bar{\lambda}\bar{p}^2})^{1/2}}{\sqrt{\pi}2^n n!}\right)^{1/2} & H_n((\sqrt{2\bar{\lambda}\bar{p}^2})^{1/2}\bar{z}) \\ & \times \exp\left(-[(\sqrt{2\bar{\lambda}\bar{p}^2})^{1/2}\bar{z}]^2/2\right), \end{aligned} \tag{8.12}$$

where $H_n(x)$ are Hermite polynomials[110] and $n = 0,\ 1,\ 2, \ldots$. The $\alpha$ parameter reduces to

$$\alpha_{HO} = \frac{1}{2\sqrt{2\bar{\lambda}\bar{p}^2}} - \frac{1}{2}. \tag{8.13}$$

One of the primary features of the HO model system is the discrete $z$ energy spectrum. The model can be said to mimic an atomic-like system, as it effectively is of finite size in the $z$ direction.

As a part of the thesis work a computer program was written specifically for this limit. In contrast to Mathieu functions, Hermite polynomials can be computed without having to resort to solving differential equations. Comparing MG data in the HO limit and data for the pure HO thus gave an extra check on the numerical procedure.

## 8.4 Investigation of the Kinetic Energy Density

In the following we use the MG model system to study the power expansion of the *non-interacting kinetic energy density*. Although the power expansion of this quantity is already well known, the procedure provides a test 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 paper 1 of part III.

The kinetic energy density $\tau(\mathbf{r})$ is a localized version of the total kinetic energy of the non-interacting Kohn–Sham system $T_s$ defined in Eq. (3.1). Similar to the implicit definition of the exchange-correlation energy per particle Eq. (4.2), one defines the kinetic energy density implicitly as

$$T_s[n] = \int \tau(\mathbf{r})d\mathbf{r}. \tag{8.14}$$

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

$$\tau(\mathbf{r}) = \left(\frac{\hbar^2}{2m_e}\right)\sum_\nu |\nabla\phi_\nu(\mathbf{r})|^2, \tag{8.15}$$

where the sum is taken over all occupied orbitals. It is known[111–113] that the second order gradient expansion of this quantity is

$$\tau_{\exp}(\mathbf{r}) = \tau_{\mathrm{LDA}} \left(1 + \frac{5}{27}s^2 + \frac{20}{9}q\right), \tag{8.16}$$

$$\tau_{\mathrm{LDA}}(\mathbf{r}) = \frac{3}{5}(3\pi^2)^{2/3} \left(\frac{\hbar^2}{2m_e}\right) n(\mathbf{r})^{5/3}. \tag{8.17}$$

The Kohn–Sham orbitals corresponding to the MG family of densities can be inserted into Eq. (8.15) to compute numerical values of the kinetic energy density. The computed values in the limit of slowly varying densities are then expected to behave accordingly to Eq. (8.16). We can verify this expected behavior 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 electron densities.

Given Eq. (8.16), the following limits are expected for the MG:

$$\text{for } s^2 = 0,\ 1/\alpha \to 0: \quad \left(\frac{\tau(\mathbf{r})}{\tau_{\mathrm{LDA}}} - 1\right)/q \to \frac{20}{9}, \tag{8.18}$$

$$\text{for } q = 0,\ 1/\alpha \to 0: \quad \left(\frac{\tau(\mathbf{r})}{\tau_{\mathrm{LDA}}} - 1\right)/s^2 \to \frac{5}{27}. \tag{8.19}$$

To evaluate these limits numerically using MG densities, values of $\tau(\mathbf{r})$ must be computed for some space point $\mathbf{r}$ for a series of values of $\alpha$. The first limit requires the use of space points where $s^2 = 0$. This requirement is fulfilled at the minimum point of the effective potential, i.e., $z = 0$, due to the symmetries of the system. The second limit requires space points where $q = 0$. A search was implemented in the computer program to numerically find a point where $q = 0$ for every value of $\alpha$.

Data for the two limits were computed and are plotted in Figs. 8.1 and 8.2. The limits as predicted by Eqs. (8.18) and (8.19) are correctly reproduced when $1/\alpha \to 0$. Apart from this expected result, it is interesting to note the behavior of the KE density at higher $1/\alpha$. One can compare the KE figures to the figures of other DFT quantities (as plotted in paper 1 of part III). These quantities are strongly influenced at values of $\alpha$ where the chemical potential enters a new $z$ dimension energy band (i.e., where $\alpha$ is an integer, and thus $1/\alpha = 1/2$ and $1/\alpha = 1/3$, etc). A similar correspondence between the energy structure and the behavior of the plotted curves is seen also for the KE density, but less pronounced.

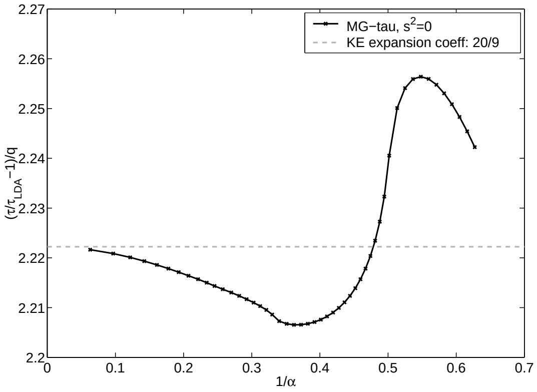

**Figure 8.1.** The quantity $(\tau(\mathbf{r})/\tau_{\rm LDA} - 1)/q$ vs $1/\alpha$ for $\bar{\lambda}/\bar{p}^2 = 0.8$ and $s^2 = 0$. In the limit of slowly varying densities, $1/\alpha \to 0$, this quantity approaches the Laplacian coefficient in the kinetic energy density power expansion, Eq. (8.16), as is expected.

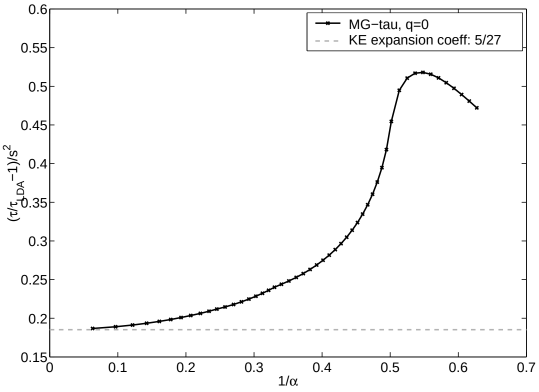

**Figure 8.2.** The quantity $(\tau(\mathbf{r})/\tau_{\rm LDA} - 1)/s^2$ vs $1/\alpha$ for $\bar{\lambda}/\bar{p}^2 = 0.8$ and $q = 0$. In the limit of slowly varying densities, $1/\alpha \to 0$, this quantity approaches the gradient coefficient in the kinetic energy density power expansion, Eq. (8.16), as is expected.

Chapter 9

# A LOCAL EXCHANGE EXPANSION

> *I seldom end up where I wanted to go,*
> *but almost always end up where I need to be.*
>
> Douglas Adams

Much of papers 1 and 3 of part III deal with the expansion of the *local* exchange energy per particle in the electron density variation. Such an expansion is expected to be useful for treating slowly varying electron densities beyond LDA in a subsystem functional scheme. The most important findings of these papers in this context are outlined here.

## 9.1 The Non-existence of a Local GEA for Exchange

Section 5.4 discussed the gradient expansion approximation (GEA). It was explained that an expansion of the exchange energy per particle in the limit of slowly varying densities, taking symmetries into account, leads to the following expression:

$$\hat{\epsilon}_x = \hat{\epsilon}_x^{\mathrm{LDA}}(n(\mathbf{r}))\Big(1 + \hat{a}_x s^2 + \hat{b}_x q + \ldots\Big). \tag{9.1}$$

Paper 1 of part III uses the Mathieu gas model system to evaluate the conventional exchange energy per particle in the limit of slowly varying Mathieu gas densities. In doing so, it is explicitly demonstrated that a general expansion on this form cannot exist! The conventional exchange energy per particle is thus a non-analytical function of $s^2$ and $q$ in the limit of slowly varying densities. The paper gives three suggestions for how to deal with this issue:

1. One can take into account the fact that the conventional exchange energy per particle is non-analytical in the limit of slowly varying electron densities, and create an expansion on a form alternative to the traditional GEA of Eq. (9.1).

2. One can utilize the freedom of choice in the exchange energy per particle (discussed in section 4.1) to transform the expression into one that is analytical and well-behaved in the limit of slowly varying electron densities. The motivation behind this idea is that an expansion on the GEA form is proved to exist for the non-local exchange expression that has been integrated by parts to fully remove the Laplacian term (or, at least it is widely believed that this expansion exists; the coefficient of the gradient term has been confirmed by several works to be 10/81; see section 5.4). However, since a functional based on the transformed exchange will use a specific non-local choice of the exchange energy per particle, all subsystem functionals used together with such a functional must also approximate that same specific choice.

3. The separation of exchange-correlation into exchange and correlation is arbitrary in DFT. The DFT exchange is defined as an imitation of the exchange expression of Hartree–Fock theory. But since this definition causes trouble, it is reasonable to reexamine it.

## 9.2 Alternative Separation of Exchange and Correlation

Paper 3 of part III shows that the gradient expansion form of Eq. (9.1) is reestablished when the Coulomb interaction in the definition of exchange Eq. (4.22) is screened. Motivated by this observation, it was suggested that the exchange part can be *redefined* to include a finite screening of the Coulomb interaction. The correlation part, defined as exchange-correlation minus exchange, is then also redefined correspondingly; the exchange and correlation sum is left unmodified.

The view here, that the definition of the exchange part can be redefined to include screening, is fundamentally different from the view present in most other works that employ screened exchange. The most common use of screening is as a temporary means to help analytical manipulation of the exchange expressions. In that case it is always with the intent of taking the limit of zero screening in the end. Other works discuss screening as an approximation of the conventional exchange. The procedure suggested here is more similar to recent works that discuss splitting the exchange into a short and a long-range contribution[114–119].

## 9.3 Redefining Exchange

To define the screened exchange energy per particle, we take the unscreened expression Eq. (4.22) and insert a Yukawa screening factor with a *Yukawa wave vector* $k_\mathrm{Y}$,

$$\hat{\epsilon}_{(x+\mathrm{Y})}([n];\mathbf{r}) = \frac{1}{2}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\int \frac{\hat{n}_x(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}e^{-k_\mathrm{Y}|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{9.2}$$

Similar to how regular exchange and correlation was defined, a correlation part corresponding to the screened exchange part is defined from the requirement that the parts sum up to the correct exchange-correlation,

$$\hat{\epsilon}_{xc}([n];\mathbf{r}) = \hat{\epsilon}_{(c-\mathrm{Y})}([n];\mathbf{r}) + \hat{\epsilon}_{(x+\mathrm{Y})}([n];\mathbf{r}). \tag{9.3}$$

An analogous way of viewing the redefinition of exchange is as a redistribution of a positive term from correlation into exchange:

$$\hat{\epsilon}_{\mathrm{Y}} = \frac{1}{4}\left(\frac{e_c^2}{4\pi\epsilon_0}\right)\int \frac{|n_1(\mathbf{r},\mathbf{r}')|^2}{n(\mathbf{r})}\frac{1-e^{-k_{\mathrm{Y}}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{9.4}$$

$$\hat{\epsilon}_{(x+\mathrm{Y})} = \hat{\epsilon}_x + \hat{\epsilon}_{\mathrm{Y}}, \quad \hat{\epsilon}_{(c-\mathrm{Y})} = \hat{\epsilon}_c - \hat{\epsilon}_{\mathrm{Y}}. \tag{9.5}$$

The main point here is that the form of $\hat{\epsilon}_{\mathrm{Y}}$ is chosen specifically to make the exchange part well-behaved in the limit of slowly varying densities.

Arbitrarily screening the exchange does not in itself guarantee a well-behaved exchange energy per particle in the limit of slowly varying densities. The screening parameter is chosen to be a function of spatial coordinate (or rather, a function of the electronic density, which varies with spatial coordinate) and must approach the following expression in the limit of slowly varying densities:

$$k_{\mathrm{Y}} = p_F \bar{k}_{\mathrm{Y}}, \tag{9.6}$$

where $\bar{k}_{\mathrm{Y}}$ is a dimensionless non-zero positive scalar constant that can be freely chosen and $p_F$ is the *position-dependent Fermi momentum*, $p_F = (2m_e/\hbar^2)^{1/2}\sqrt{\mu - v_{\mathrm{eff}}(\mathbf{r})}$. In the limit of slowly varying densities, $p_F \to (3\pi^2 n)^{1/3}$.

## 9.4 An LDA for Screened Exchange

Paper 3 of part III derives an LDA for screened exchange. The method is basically the same as for the derivation of the regular LDA in section 5.2, but uses the screened exchange expressions. The result is

$$\hat{\epsilon}^{\mathrm{LDA}}_{(x+\mathrm{Y})}(n(\mathbf{r})) = \hat{\epsilon}^{\mathrm{LDA}}_x(n(\mathbf{r}))I_0(\bar{k}_{\mathrm{Y}}), \tag{9.7}$$

where $I_0(\bar{k}_{\mathrm{Y}})$ is a complicated function of $\bar{k}_{\mathrm{Y}}$,

$$I_0(\bar{k}_{\mathrm{Y}}) = \frac{1}{24}\Big(24 - 4\bar{k}_{\mathrm{Y}}^2 - 32\bar{k}_{\mathrm{Y}}\arctan(\frac{2}{\bar{k}_{\mathrm{Y}}}) + \bar{k}_{\mathrm{Y}}^2(12 + \bar{k}_{\mathrm{Y}}^2)\ln(\frac{4}{\bar{k}_{\mathrm{Y}}^2} + 1)\Big). \tag{9.8}$$

If the screened LDA exchange expression is subtracted from the total exchange-correlation energy per particle for the uniform electron gas, the remainder can be parameterized as a function of the electron density. The result is a parameterization of the modified correlation that is compatible with the screened exchange LDA. Such an parameterization was done in paper 3 of part III to produce two screened LDA expressions, YLDA1 and YLDA2. The specifics of their construction shows that the parameterization is at least no more complicated than for regular correlation. Hence, the modified correlation does not in itself complicate functional development. In fact, since the screening has eliminated an artificial complication in exchange that is not present in exchange-correlation, the modified correlation may even be more well-behaved than regular correlation.

It is possible to take benefit of parameterizations of the modified correlation, such as YLDA1 and YLDA2, even when a traditional correlation is needed. A parameterization of the modified correlation $\hat{\epsilon}^{\mathrm{LDA}}_{(c-\mathrm{Y})}(n(\mathbf{r}))$ can be turned into a regular LDA correlation parameterization $\hat{\epsilon}^{\mathrm{LDA}}_{c}(n(\mathbf{r}))$ and vice versa;

$$\hat{\epsilon}^{\mathrm{LDA}}_{c}(n(\mathbf{r})) = \Big(\hat{\epsilon}^{\mathrm{LDA}}_{(x+\mathrm{Y})}(n(\mathbf{r})) + \hat{\epsilon}^{\mathrm{LDA}}_{(c-\mathrm{Y})}(n(\mathbf{r}))\Big) - \hat{\epsilon}^{\mathrm{LDA}}_{x}(n(\mathbf{r})) \tag{9.9}$$

and conversely,

$$\hat{\epsilon}^{\mathrm{LDA}}_{(c-\mathrm{Y})}(n(\mathbf{r})) = \Big(\hat{\epsilon}^{\mathrm{LDA}}_{x}(n(\mathbf{r})) + \hat{\epsilon}^{\mathrm{LDA}}_{c}(n(\mathbf{r}))\Big) - \hat{\epsilon}^{\mathrm{LDA}}_{(x+\mathrm{Y})}(n(\mathbf{r})). \tag{9.10}$$

The latter relation makes it possible to use a regular LDA parameterization in a screened exchange scheme. However, in that case one does not make use of the properties of the modified correlation, and thus is limited by the accuracy of the parameterization of the regular correlation.

## 9.5 A GEA for Screened Exchange

Paper 3 of part III also derives a GEA for the local screened exchange. It was discussed in section 5.4 how several works that dealt with the non-local GEA derived an incorrect coefficient due to the (sometimes covert) use of screening. One starts from an intermediate step in one of these works[63] where no non-local transformations have yet been made, and then makes sure to keep the screening finite throughout the derivation. The end result is

$$\hat{\epsilon}_x = \hat{\epsilon}^{\mathrm{LDA}}_{(x+\mathrm{Y})}(n(\mathbf{r}))\Big(1 + \hat{a}_{(x+\mathrm{Y})}s^2 + \hat{b}_{(x+\mathrm{Y})}q\Big), \tag{9.11}$$

where

$$\hat{a}_{(x+\mathrm{Y})} = \frac{8}{27}\left(\frac{3}{4} - \frac{1}{3}\frac{I_B(\bar{k}_\mathrm{Y})}{I_0(\bar{k}_\mathrm{Y})} + \frac{1}{2}\frac{I_C(\bar{k}_\mathrm{Y})}{I_0(\bar{k}_\mathrm{Y})}\right), \tag{9.12}$$

$$\hat{b}_{(x+\mathrm{Y})} = \frac{8}{27}\frac{I_B(\bar{k}_\mathrm{Y})}{I_0(\bar{k}_\mathrm{Y})} - \frac{4}{9}, \tag{9.13}$$

and

$$I_B = \frac{40 + 12\bar{k}_\mathrm{Y}^2 - 6\bar{k}_\mathrm{Y}(4+\bar{k}_\mathrm{Y}^2)\arctan(2/\bar{k}_\mathrm{Y}) - (4+\bar{k}_\mathrm{Y}^2)\ln(4/\bar{k}_\mathrm{Y}^2+1)}{16 + 4\bar{k}_\mathrm{Y}^2}, \tag{9.14}$$

$$I_C = \frac{\bar{k}_\mathrm{Y}(4+\bar{k}_\mathrm{Y}^2)\arctan(2/\bar{k}_\mathrm{Y}) - 4 - 2\bar{k}_\mathrm{Y}^2 - 2(\bar{k}_\mathrm{Y}^2-4)/(\bar{k}_\mathrm{Y}^2+4)}{8 + 2\bar{k}_\mathrm{Y}^2}. \tag{9.15}$$

In the paper, these expressions were also confirmed numerically using a screened Mathieu gas model.

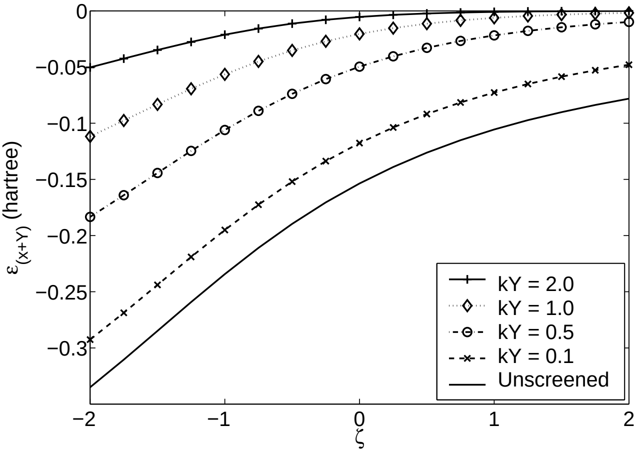

**Figure 9.1.** The screened Airy gas for different screening parameters $\bar{k}_{\mathrm{Y}}$.

## 9.6 The Screened Airy Gas

If screened exchange is used to derive the exchange expression for the Airy gas of section 7.6, one arrives at

$$\hat{\epsilon}^{\mathrm{Airy}}_{(x+\mathrm{Y}),0} = \frac{-1}{\pi n_0} \int_{-\infty}^{\infty} d\zeta' \int_0^{\infty} d\chi \int_0^{\infty} d\chi' \, \frac{g_{\mathrm{Y}}(\sqrt{\chi}\Delta\zeta, \sqrt{\chi'}\Delta\zeta, \bar{k}_{\mathrm{Y}}\Delta\zeta)}{\Delta\zeta^3} \times \mathrm{Ai}(\zeta+\chi)\mathrm{Ai}(\zeta'+\chi)\mathrm{Ai}(\zeta+\chi')\mathrm{Ai}(\zeta'+\chi'), \tag{9.16}$$

where

$$g_{\mathrm{Y}}(\eta, \eta', \chi) = \eta\eta' \int_0^{\infty} \frac{J_1(\eta t) J_1(\eta' t)}{t\sqrt{1+t^2}} e^{-\chi\sqrt{1+t^2}} dt. \tag{9.17}$$

The same computational procedure as for the regular Airy gas yields the data shown in Fig. 9.1. Some preliminary work have been done for producing a parameterization of the screened Airy exchange.

## Chapter 10

# INTRODUCTION TO THE PAPERS

> *Perfection is achieved, not when there is nothing more to add, but when there is nothing left to take away.*
>
> Antoine de Saint Exupéry

### Paper 1: Subsystem functionals in density-functional theory: Investigating the exchange energy per particle.

The paper presents the subsystem functional approach and examines properties of a suggested form of a subsystem functional for subsystems with slowly varying electron densities. A main result, relevant also outside the context of subsystem functionals, is that the expansion of the local exchange energy per particle is ill defined. The fact that the expansion is ill defined was demonstrated through explicit computation for model systems. The paper goes into much detail of the Mathieu gas model system, which is necessary to make a careful data analysis. In an appendix, the paper gives many details on the construction of the computer program used to generate the data.

I wrote the computer programs and performed the calculations. My coauthor and I did the data analysis and theory discussions together. I wrote the first draft of the paper, and then my coauthor and I completed it jointly.

### Paper 2: How to Tell an Atom From an Electron Gas: A Semi-Local Index of Density Inhomogeneity.

The paper discusses the construction of indices to categorize regions of the electron density. Such indices are necessary in a subsystem functional approach for specifying the interpolation between functionals used within a system. The paper discusses the problem of distinguishing regions of the density pertaining to atoms from slowly varying gas-like regions. A main result is that to avoid any confusion between the two classes of density regions, a rather complicated expression is needed that involves higher order derivatives of the electron and kinetic energy densities.

I took part in discussions of the ideas and results. I wrote the computer program for performing the tests of the indices in the Mathieu gas. I wrote the part of the paper that is about the Mathieu gas tests.

### Paper 3: Alternative separation of exchange and correlation in density-functional theory.

The paper presents a method to create an exchange functional for partial regions where the electron density is slowly varying. The part of the exchange energy that causes the expansion of the local exchange energy per particle to be ill-defined is separated out and instead added to the correlation energy. The new 'revised' exchange quantity is demonstrated to be numerically well behaved. Its second order GEA is derived, which provides a functional for slowly varying electron densities. Furthermore, a local density approximation is constructed based on the revised exchange and correlation.

I wrote the computer program, performed the calculations and created the figures. My coauthor and I did the data analysis and theory discussions together. I wrote the first draft of the paper, and then my coauthor and I completed it jointly.

### Paper 4: Functional designed to include surface effects in self-consistent density functional theory

This paper constructs a functional using the subsystem functional scheme. The functional automatically partitions the electron density into surface and interior regions and applies suitable approximations in either part. Successful test results of the functional in electronic structure calculations of aluminum, platinum and silicon are presented.

I implemented the functional in the pseudopotential generation program, which involved extending the software with routines for numerical functional derivatives. I implemented the functional in the DFT program. Calculations of the bulk test results and the jellium XC surface energies were performed by me. Preparation for the vacancy tests were done jointly. My coauthor and I did the data analysis and theory discussions together. I wrote the first draft of the paper, and then my coauthor and I completed it jointly.

### Paper 5: PBE and PW91 are not the same

The paper is a comment on an unexpected feature seen in the test data of Paper 4. It is common practice to regard the PBE functional as basically equivalent to the PW91 functional, but with a simpler derivation. However, we discovered that for metal vacancies and jellium surface energies, the two functionals perform more differently than expected. We present a model that relates the difference in vacancy formation energies to the difference in jellium formation energies.

I did the main work on the model relating jellium and vacancy results and created the figures. I wrote the first draft of the paper, and then the coauthors completed it jointly.

### Paper 6: Numerical integration of functions originating from quantum mechanics

This paper is a technical report on an algorithm for parallel integration used for some of the data presented in Paper 1. All work and the writing of the report were made by me.

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*At the all-you-can-eat buffet, the only obstacle is yourself.*

Scott Adams, in the comic Dilbert

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R. Armiento

Rickard Armiento,
Stockholm, 30 Aug 2005

## Appendix A

# UNITS

The form of some equations depends on the choice of units in which they are expressed. This thesis uses SI units, but in the papers the use of unit systems varies. To avoid confusion because of the differing practices, a brief summary of the relevant unit systems follows.

## A.1 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;

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

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

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

Some presentations stop here, because this is enough to get rid of the most common prefactors of quantum mechanical equations, simplifying them significantly. However, it is not unusual also to make a set of other quantities dimensionless and equal to 1. One sets

$$e_c = 1 \;\Leftrightarrow\; \frac{1}{4\pi\epsilon_0} = 1, \quad m_e = 1 \;\Leftrightarrow\; \hbar = 1. \tag{A.3}$$

This practice is consistent with Hartree's own use of this unit system[120] in 1927. A common alternative notation for expressing the use of full hartree units is

$$\hbar = m_e = e_c = 1, \tag{A.4}$$

where $1/(4\pi\epsilon_0) = 1$ is assumed, i.e., one starts from the cgs-esu system (see below). Numerical values of quantities of other dimensions than mass, charge, energy and length are then usually marked as given in "a.u.", designating atomic units. Giving the values with no unit at all is also formally correct.

## A.2 Rydberg Atomic Units

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

$$\frac{1}{2}\frac{m_e e_c^4}{(4\pi\epsilon_0)^2\hbar^2} = 1 \text{ rydberg}. \tag{A.5}$$

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

$$\frac{\hbar^2}{2m_e} = 1. \tag{A.6}$$

As for hartree atomic units, some presentations stop here; but it is also common to set

$$e_c^2 = 2 \;\Leftrightarrow\; \frac{1}{4\pi\epsilon_0} = 1, \quad m_e = \frac{1}{2} \;\Leftrightarrow\; \hbar = 1. \tag{A.7}$$

A common alternative notation for expressing the use of full rydberg units is

$$\hbar = 1,\; e_c^2 = 2,\; m_e = 1/2. \tag{A.8}$$

## A.3 SI and cgs Units

The cgs and SI systems of units are based on similar ideas within dimensions of mass, time and length but they differ significantly in the area of electromagnetism. There are 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 $\mu_0 = 1/(\epsilon_0 c^2) = 1$ thus giving $\epsilon_0 = 1/c^2$.

## A.4 Conversion Between Unit Systems

To convert a mathematical formula from SI or cgs to atomic units, one sets the physical constants to their respective dimensionless numerical values in the atomic unit system. The same procedure is used for converting from SI to cgs.

To convert from atomic units to SI or cgs one identifies the unit that the mathematical formula is supposed to have in SI or cgs. Then one combines the dimensionless quantities of the atomic unit system into a factor that 1) is equal to the value 1 in the atomic unit system, and 2) has the unit the formula is supposed to have in SI or cgs units. The expression is then multiplied with this factor. The same procedure is used for converting from cgs to SI. The factor to use in the latter conversion is, of course, dependent on the kind of cgs system one is working with, which, if unknown, must be determined for example by observing the appearance of a Coulomb factor in an equation where it is known that such a factor should appear.

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