# Spinor-orbital functionals and the optimized effective potential method

## Dissertation

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**Stefano Pittalis**

Institut für Theoretische Physik
Freie Universität Berlin

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## Dedication

*To my parents, Teresa and Pietro.*

*And in memory of my grandfather*
*Salvatore Pittalis.*

# Abstract

The description of systems of interacting electrons in the presence of magnetic fields within density-functional theory requires the current and magnetization densities to be used as basic variables besides the particle density. However, electron-gas-based approximations for the exchange and correlation energies exhibit derivative discontinuities as a function of the magnetic field whenever a new Landau level is occupied, which makes them impractical to use as local approximation. The same approximations also assume a collinear configuration respectively between the magnetization, vorticity density and corresponding conjugate fields. Orbital dependent functionals – which depend on Kohn-Sham spinors – allow to overcome both limitations. To make use of such expressions, we have derived the integral equations for the exchange-correlation components of the scalar and vector potential, and the magnetic field in the fashion of the optimized effective potential method. We suggest a practical scheme for their solution as well as a simplifying approximation. The formalism is then applied to several systems and problems: we consider the degeneracy problem for open-shell atoms; orbital magnetic moments and band-splittings induced by spin-orbit coupling for extended systems are calculated; and quantum dots in an external magnetic field are studied. The exact-exchange functional is employed both in collinear and non-collinear fashion within density-functional theory, spin-density-functional theory and current-spin-density-functional theory. The effect of the exchange vector potential is verified to be minor. An expression for the Colle and Salvetti approximation for the correlation energy has been derived which explicitly includes orbital currents and their relevance has been verified. New orbital and density functionals for the exchange energy of two-dimensional systems are proposed, which are seen to perform significantly better than the corresponding local-spin-density approximation in two-dimensional systems with few electrons.

# Kurzfassung

Die Beschreibung von Systemem wechselwirkender Elektronen in magnetischen Feldern im Rahmen der Dichtefunktionaltheorie erfordert die Verwendung der Strom- und Magnetisierungsdichten als zusätzliche fundamentale Variablen neben der Teilchendichte. Für ein homogenes Elektronengas im äußeren Magnetfeld weist die Austausch-Korrelationsenergie immer dann Ableitungsunstetigkeiten als Funktion des Magnetfelds auf, wenn ein neues Landau-Niveau mit Elektronen besetzt wird. Im Rahmen einer auf diesem Modell beruhenden Lokaldichtenäherung führt dies zu von lokalen Werten der Dichte bestimmten Unstetigkeiten der entsprechenden Austausch-Korrelationspotentiale, die die Lokaldichtenäherung in numerischen Anwendungen unpraktikabel macht. Des weiteren nimmt man in der Lokaldichtenäherung eine kollineare Konfiguration zwischen der lokalen Magnetsierungs- bzw. Vortizitätsdichte und den entsprechenden konjugierten Potentialen an.

Mit Hilfe von Funktionalen, die explizit von Kohn-Sham Spinororbitalen abhängen, kann man beide Einschränkungen überwinden. Zur Anwendung solcher Funktionale wird hier eine Verallgemeinerung der sogenannten Methode des Optimierten Effektiven Potentials vorgestellt und die entsprechenden gekoppelten Integralgleichungen für die Austausch-Korrelationspotentiale (skalares Potential, Magnetfeld und Vektorpotential) hergeleitet. Ein praktisches Verfahren zu ihrer Lösung sowie eine vereinfachende Näherung werden vorgeschlagen. Anwendungen des Formalismus für verschiedene Systeme und Probleme werden untersucht: wir betrachten das Problem entarteter Grundzustände bei Atomen mit offenen Schalen; magnetische Orbitalmomente und spin-bahn-induzierte Bandaufspaltungen für ausgedehnte Festkörper werden berechnet; Quantenpunkte im externen Magnetfeld werden untersucht. Bei diesen Anwendungen wird das exakte Austauschfunktional sowohl in kollinearer als auch in nicht-kollinearer Situation im Rahmen der Dichte-, Spindichte- und Stromdichtefunktionaltheorie verwendet. In allen Beispielen zeigt sich, daß der Effekt des Austausch-Vektorpotentials gering ist.

Für die Korrelationsenergie wird eine Verallgemeinerung des Colle-Salvetti-Funktionals hergeleitet, die Orbitalströme explizit berücksichtigt, und der Effekt dieser Ströme wird untersucht. Weiterhin werden neue Orbital- und Dichtefunktionale für die Austauschenergie zweidimensionaler Systeme vorgeschlagen und es wird gezeigt, daß diese für Systeme mit wenigen Elektronen deutlich verbesserte Ergebnisse im Vergleich zur 2D-Lokaldichtenäherung liefern.

# Contents

# List of Figures

# List of Tables

# Abbreviations

| | |
|---|---|
| **CEDA** | Common Energy Denominator Approximation |
| **CSDFT** | Current Spin Density Functional Theory |
| **DFT** | Density Functional Theory |
| **EXX** | EXact eXchange |
| **GGA** | Generalized Gradient Approximation |
| **HF** | Hartree-Fock |
| **HK** | Hohenberg Kohn |
| **KLI** | Krieger, Li, Iafrate |
| **KS** | Kohn and Sham |
| **LDA** | Local Density Approximation |
| **LSDA** | Local Spin Density Approximation |
| **LVA** | Local Vorticity Approximation |
| **OEP** | Optimized Effective Potential |
| **SCDFT** | Spin Current Density Functional Theory |
| **SDFT** | Spin Density Functional Theory |
| **SIC** | Self Interaction Correction |
| **xc** | eXchange and Correlation |

# Chapter 1

# General introduction

At present, the general and practical solution of the quantum mechanical many-body problems for interacting electrons remains unsolved. An ingenious and in principle exact way of approaching the problem is density functional theory (DFT). With the introduction of the Kohn-Sham scheme, the interacting problem for the ground state is mapped onto a problem for the ground state of a non-interacting auxiliary system.

In this way, the challenge is translated to find *practical* and *universal* expressions for the quantities that incorporate all the complications of the original, interacting problem: the Pauli and Coulomb correlation (or exchange-correlation) energy functionals. The approximations to these quantities should be practical enough to be easily, economically and routinely applied. Moreover, they should be universal to perform equally well for all the systems one might want or need to study.

Nowadays, density-functional theory is the cornerstone of electronic structure calculations for atoms, molecules, solids and nanostructures. But failures and limitations exist as well. At the same time, there is the need to extend the formalism, and the corresponding schemes of calculations, to deal with more and more diverse situations. Often, these two issues meet each other along the way of new advances.

At the center of this thesis is the aim of dealing with the ground state of electrons with non-vanishing current and or non-vanishing magnetization. Thus we resort to the generalization of DFT known as spin-DFT (SDFT) and current-SDFT (CSDFT). In this context, we consider a particular class of approximations for the exchange-correlation energies, generally known as orbital functionals. This is mainly motivated by two facts. First, there is the need to overcome the numerical problems which arise in the application of the local density approximations for the exchange-correlation energies of CSDFT. Second, most approximations in SDFT and CSDFT have the shortcoming that they assume a collinear configuration between the magnetization, vorticity density and corresponding magnetic field.

This thesis devides in two parts: Chaps. 2-4 serve as introduction to the foundation of DFT as well as orbital functionals; Chaps. 5-8 report new advances and results.

In Chap. 2, the basic ideas and main formulations of DFT are introduced. Approximations for the exchange-correlation energy functional in terms of orbital functionals are reviewed in Chap. 3. Chap. 4 focusses on the fact that, in principle, the description of many-electron systems in the presence of a magnetic field within a density-functional framework requires the paramagnetic current density and magnetization density to be used as basic variables besides the electron density. Here, we also analyze the relations, similarities and differences among several possible formulations of DFT. This conclude the general review.

Extensions of the optimized effective potential (OEP) method for functionals depending explicitly on the Kohn-Sham spinors are reported in Chap. 5. With these extensions the equations providing the exchange-correlation fields are derived. We propose a practical scheme for their solution, and a simplifying approximation which we analyze in more detail.

The formalism developed in the previous chapter is then applied in Chap. 6 to shed light on a long standing problem of density functioanl theory, which is known as "the degeneracy problem". With this respect, open-shell atoms at vanishing external magnetic field are investigated. The aim is to properly describe the degeneracy of the ground states with and without a current. An analysis at the level of the exchange-only approximation is carried out. This is followed by a new analysis of the Colle and Salvetti correlation functional to account for the orbital currents and the relevance of these currents is evaluated.

Different systems are analyzed in Chap. 7. In particular, the orbital magnetic moments and band-splittings induced by the spin-orbit coupling in several solids and non-collinear magnets are investigated. Two-dimensional (2D) quantum dots exposed to external magnetic fields are considered.

Motivated by the fact that approximate exchange-correlation energy functionals for three-dimensional systems perform poorly when applied to 2D systems, new and efficient implicit and explicit density functionals for the exchange energy in 2D are derived and applied in Chap. 8.

General conclusions are drawn in Chap. 9.

# Chapter 2

# Density functional theory

A reformulation of the interacting many-electron problem in terms of the electron density rather than the many-electron wavefunction has been attempted since the early days of quantum mechanics. The advantage is clear. While the wavefunction for interacting electrons depends in a complex fashion on all the particle coordinates, the particle density is a function of only three spatial coordinates. Initially, like in the Thomas-Fermi method [1, 2], it was believed that formulating quantum mechanics solely in terms of the particle density is only approximate. However, in the mid-60s, Hohenberg and Kohn [3] showed that in principle, for systems of electrons acted upon by an electrostatic potential, it is possible to determine exactly all the properties of the many-electron ground state from knowledge of the corresponding ground state particle density alone. Also early in the development of quantum mechanics it appeared another important approach to the many-particle problem consisting in the single-particle approximation. Here, the two-particle potential representing the interaction between particles is replaced by some effective one-particle potential. A prominent example of this approach is the Hartree-Fock method, which however includes in the effective one-particle potential only the exchange contributions. A year after the Hohenberg-Kohn theorem had been proved, Kohn and Sham [4] made a step forward by showing that, taking the ground state particle density as basic quantity, both the exchange and correlation effects due to the electron-electron interaction can be treated through a single-particle Schrödinger equation in a well defined sense. The Hohenberg-Kohn theorem and Kohn-Sham scheme are the basic elements of density-functional theory (DFT). Here we will review them, going from the initial formulation, dealing with only non-degenerate ground states, till the extension to degenerate ground states. Also we briefly consider alternative and/or more rigorous mathematical formulations of the same theory.

## 2.1 Introduction

The non-relativistic Hamiltonian for interacting electrons moving in a static potential $v(\mathbf{r})$ reads (in atomic units)

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V} := -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} v(\mathbf{r}_i). \tag{2.1}$$

Here, $\hat{T}$ is the total kinetic-energy operator, $\hat{V}_{ee}$ describes the interaction between the electrons, and $\hat{V}$ is a local (multiplicative) scalar operator, which includes the interaction of the electrons with the nuclei (which are considered within the Born-Oppenheimer approximation as fixed points) and possibly other external scalar potentials.

The eigenstates, $\Psi_E(x_1, ..., x_N)$, of the system are obtained by solving the eigenvalue problem

$$\hat{H}\Psi_E(x_1, ..., x_N) = E\Psi_E(x_1, ..., x_N), \tag{2.2}$$

with appropriate boundary conditions specifying the physical problem at hand. $x_i$ stands for both the space- and spin-coordinates $(\mathbf{r}_i, s_i)$. Eq. (2.2) is the time-independent Schrödinger equation. We are particularly interested in the ground state, which is the eigenstate with lowest energy. Also, we will assume that the wavefuntion can be normalized.

Due to the interactions among the electrons, $\hat{V}_{ee}$, an explicit and closed solution of the many-electrons problem (2.2) is, in general, not possible. On the other hand, a wide range of physical and chemical phenomena can be understood only as a manifestation of the interactions among the electrons. For this reason, we are also interested in obtaining approximate, but accurate, solutions.

We observe that once the number of electrons in the system is given (and knowing, of course that they interact via the Coulomb interaction) the Hamiltonian is then determined by specifying the external potential. For a given external potential, $v(\mathbf{r})$, we then introduce the total energy as a functional of the (normalized) many-body wavefunction $\Psi(x_1, ..., x_N)$

$$E_v[\Psi] = \langle\Psi|\hat{T} + \hat{V}_{ee} + \hat{V}|\Psi\rangle. \tag{2.3}$$

The energy functional (2.3) may be evaluated for any $N$ electron wavefunction, and the Rayleigh-Ritz variational principle ensures that the ground state energy, $E_v$, is given by

$$E_v = \inf_{\Psi,\ \langle\Psi|\Psi\rangle=1} E_v[\Psi]\ . \tag{2.4}$$

The Euler equation expressing the minimum of the energy is

$$\frac{\delta}{\delta\Psi}\left\{E_v[\Psi] - \lambda\left[\langle\Psi|\Psi\rangle - 1\right]\right\} = 0. \tag{2.5}$$

Relation (2.5) again leads to the many-body Schrödinger equation and the Lagrangian multiplier $\lambda$ can be identified with the energy. Now, with the variational principle at hand, we have gained a procedure to obtain approximate solutions. This is done by restricting the form of the wavefunctions to a particular form. In the Hartree-Fock (HF) approximation, for example, the form of the wave-function is restricted to a single Slater determinant. The Euler equation (2.5), along with the constraint for the single-particle orbitals to be orthonormal, yields the so-called HF equation. This equation has the form of a Schrödinger equation for non-interacting electrons in an effective non-local potential. The HF Slater determinant is then used to obtain the total energy from expression (2.3). The estimation of the energy obtained in this way is said to be accurate up to within the exchange energy. The rest is defined as the correlation energy. The approximate nature of the HF method is due to the fact that the true many-electron wavefunction is not a single determinant. However the full wavefunction can be expressed as a linear combination of an infinite number of determinants. Thus, an estimation beyond the exchange energy can be done either by adding more and more determinants or by introducing ad-hoc wavefunction models, typically having many parameters.

Unfortunately these approaches based on the wavefunctions, although accurate, are affected by an impractical growth of the numerical effort with the number of particles, and thus with the total number of the coordinates the wavefunction depends on. Hence, inspired by the Tomas-Fermi approach, one might wonder if the role played by the wavefunction could be substituted by the particle density. In that case, one would deal with a function of only three spatial coordinates, independently of the number of electrons. The definition of particle density is the following

$$n(\mathbf{r}) := \langle\Psi| \sum_{i=1}^{N} \delta(\hat{\mathbf{r}} - \hat{\mathbf{r}}_i)|\Psi\rangle = N \sum_{\sigma} \int dx_2 ... \int dx_N \Big|\Psi(\mathbf{r}, \sigma, x_2, ..., x_N)\Big|^2 \qquad (2.6)$$

from which

$$\int d^3r \; n(\mathbf{r}) = N. \qquad (2.7)$$

The assurance that the electronic density alone is enough to determine all observable quantities of the system is provided by the theorem of Hohenberg and Kohn, as exposed in the following section.

## 2.2 Hohenberg-Kohn theorem

Let us denote with $\mathbf{P}$ the set of external potentials leading to a *non-degenerate* ground state for N interacting electrons. For a given potential, the corresponding ground state, $\Psi$, is obtained through the solution of the Schrödinger equation

$$v \quad \longrightarrow \quad \Psi, \quad \text{with} \quad v \in \mathbf{P}. \qquad (2.8)$$

Wavefunctions obtained in this way are called (interacting) v-representable. We collect these ground state wavefunctions in the set $\mathbf{W}$. The corresponding particle densities can be computed using definition (2.6) as

$$\Psi \longrightarrow n, \text{ with } \Psi \in \mathbf{W}. \tag{2.9}$$

Ground state particle densities obtained in this way are said to be (interacting) v-representable. We denote the set of these densities as $\mathbf{D}$.

## First part

Given a density $n \in \mathbf{D}$, the first part of the Hohenberg-Kohn theorem states that the wavefunction $\Psi \in \mathbf{W}$ leading to $n$ is unique apart from an inessential constant phase factor. The proof is carried out by *reductio ad absurdum*.

Consider two different wavefunctions $\Psi_1$ and $\Psi_2$ in $\mathbf{W}$, in the sense that they differ by more than a simple constant phase factor. Let, furthermore, $n_1$ and $n_2$ be the corresponding densities computed by Eq. (2.6). Since, by construction, we are restricting ourselves to non-degenerate ground states, $\Psi_1$ and $\Psi_2$ have to come from two different potentials, say, $v_1$ and $v_2$ respectively. Let us assume that

$$\Psi_1 \neq \Psi_2 \text{ and } n_1(\mathbf{r}) = n_2(\mathbf{r}). \tag{2.10}$$

Application of the Rayleigh-Ritz variational principle yields the first inequality

$$\langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle, \tag{2.11}$$

from which we obtain

$$E_1 < \langle \Psi_2 | \hat{H}_2 + (\hat{V}_1 - \hat{V}_2) | \Psi_2 \rangle = E_2 + \int d^3r \; n_1(\mathbf{r}) \left[ v_1(\mathbf{r}) - v_2(\mathbf{r}) \right]. \tag{2.12}$$

Alterantively, we also have

$$E_2 < \langle \Psi_1 | \hat{H}_1 + (\hat{V}_2 - \hat{V}_1) | \Psi_1 \rangle = E_1 + \int d^3r \; n_2(\mathbf{r}) \left[ v_2(\mathbf{r}) - v_1(\mathbf{r}) \right]. \tag{2.13}$$

Assuming now that the two densities are equal, $n_1(\mathbf{r}_1) = n_2(\mathbf{r})$, and adding the inequalities (2.12) and (2.13) yields

$$E_1 + E_2 < E_1 + E_2, \tag{2.14}$$

which is a contradiction. We have to conclude that the above hypothesis (2.10) on the densities was wrong, and obtain $n_1 \neq n_2$.

The fact that the ground-state density determines the wavefunction will be denoted symbolically as

$$n \longrightarrow \Psi, \text{ with } n \in \mathbf{D} \text{ and } \Psi \in \mathbf{W}. \tag{2.15}$$

### Second part

It is also possible to verify that the elements $\Psi$ of $\mathbf{W}$ determine the elements $v$ of $\mathbf{P}$, apart from an additive constant. This can be explicitly seen by inverting the Schrödinger equation

$$\sum_{i=1,N} v(\mathbf{r}_i) = E - \frac{(T + V_{ee})\,\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)}. \tag{2.16}$$

We summarize this result by writing

$$\Psi \longrightarrow v, \text{ with } \Psi \in \mathbf{W} \text{ and } v \in \mathbf{P}. \tag{2.17}$$

## 2.2.1 Consequences

Putting together the first and second part of the theorem - Eqs. (2.15) and (2.17) - yields

$$n \longrightarrow v + const, \quad \text{with } n \in \mathbf{D} \text{ and } v \in \mathbf{P}. \tag{2.18}$$

It is now clear that the ground state particle density determines the external potential (up to an additive constant).

Moreover, from the first part of the theorem it follows that any ground-state observable is a functional of the ground-state particle density. This is seen by using the (one-to-one) dependence of the wavefunction, $\Psi[n]$, on the particle density

$$\langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle = O[n]. \tag{2.19}$$

For example, the following functional can be defined

$$E_{v,\mathrm{HK}}[n] := \langle \Psi[n] | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi[n] \rangle = F_{\mathrm{HK}}[n] + \int d^3r \; n(\mathbf{r}) v(\mathbf{r}) \tag{2.20}$$

where $v$ is a given external potential and $n$ can be any density in $\mathbf{D}$. Note that

$$F_{\mathrm{HK}}[n] := \langle \Psi[n] | \hat{T} + \hat{V}_{ee} | \Psi[n] \rangle. \tag{2.21}$$

is independent of $v$: In this sense, it is said to be a universal functional.

Let $n_0$ be the ground-state particle density of the potential $v_0$. The Rayleigh-Ritz variational principle (2.4) immediately allows one to conclude

$$E_{v_0} = \min_{n \in \mathbf{D}} E_{v_0,\mathrm{HK}}[n] = E_{v_0,\mathrm{HK}}[n_0] \tag{2.22}$$

We have finally obtained a variational principle based not anymore on the "expensive" wavefunction but on the particle density.

### 2.2.2 Extension to degenerate ground states

As demonstrated by Kohn [5, 6], the Hohenberg-Kohn theorem can be generalized to include in the set **P** local potentials having *degenerate* ground states as well. Thus, we now consider the situation where to the lowest eigenvalue of the Schrödinger equation (2.2) can correspond an entire subspace of wavefunctions. Correspondingly, the sets **W** and **D** are enlarged to include all the additional ground-state wavefunctions and particle densities.

Clearly, the solution of the Schrödinger equation (2.2) establishes a mapping from **P** to **W** which is one-to-many. Moreover, different degenerate wavefunctions can have the same particle density. Thus, the equation (2.6) establishes a mapping from **W** to **D** which is many-to-one. However, it is still possible to show that any one of the degenerate ground-state densities determine the potential uniquely.

The first part of the HK theorem needs to be modified as follows. It is first observed that two degenerate subspaces, ground states of two different potentials are disjoint. The proof is carried out by *reductio ad absurdum*:

If one assume that a common eigenstate $\Psi$ can be found, then subtraction of the Schrödinger equations yields

$$(\hat{V}_1 - \hat{V}_2)\Psi = (E_1 - E_2)\Psi. \tag{2.23}$$

For this identity to be true, the eigenstate should vanish in the region where the two potentials differ by more than an additive constant. This region has measure greater than zero. But physical eigenfunctions are expected to vanish only on set of measure equal to zero. This leads to a contradiction. So we conclude that $v_1$ and $v_2$ cannot have common eigenstates. This allows to apply the Rayleigh-Ritz variational principle (similarly to what has been done in the case of the non-degenerate case) to show that ground states from two different potentials always have different particle densities.

However, one should note that two or more degenerate ground state wavefunctions can have the same particle density. As a consequence, neither the wavefunctions nor a generic ground state property can be uniquely determined from knowledge of the ground state particle density alone. This implies that we have to reconsider the definition of the universal $F_{\mathrm{HK}}$ as well. Just below, we verify that the one-to-one correspondence among ground state wavefunctions and particle densities is not necessary to define $F_{\mathrm{HK}}$.

First, we observe that the second part of the HK theorem goes as in the original proof. We thus obtain that each ground state in a degenerate level determines the external potential up to an additive constant. Then, the first part together with the second one, again confirm that any element of **D** determines an element of **P**, up to an additive constant. In particular, any one of the degenerate densities determines the external potential. This fact, together with the trivial observation that the total energy is the same for all the wavefunctions in a given degenerate level, allow one

to define $F_{\rm HK}$ as follows

$$F_{\rm HK}[n] := E\left[v[n]\right] - \int d^3r v[n](\mathbf{r})n(\mathbf{r}) \ , \tag{2.24}$$

which implies that the value of

$$F_{\rm HK}[n] = \langle \Psi \to n|\hat{T} + \hat{V}_{ee}|\Psi \to n\rangle \tag{2.25}$$

is the same for all the degenerate ground-state wavefunctions that have the same particle density. The variational principle based on the particle density can then be formulated as before in Eq. (2.22).

## 2.3 Kohn-Sham scheme

The expressions we have obtained in the previous section defining $F_{\rm HK}$ are only formal ones. In practice, $F_{\rm HK}$ has to be approximated. To obtain approximations which yield accurate results turns out to be an extremely difficult task. However, efficient approximations can be constructed by introducing the Kohn-Sham scheme. There the idea is to extract from $F_{\rm HK}$ some parts that are exactly known (in the sense that we are going to specify).

Let us consider the Hamiltonian of N non-interacting electrons

$$\hat{H}_s = \hat{T} + \hat{V}_s := -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} v(\mathbf{r}_i). \tag{2.26}$$

Similarly to what has been done for the interacting system, we group all the external local potentials $v_s$ in the set $\mathbf{P^s}$. The corresponding non-interacting ground state wavefunctions $\Psi_s$ are then grouped in the set $\mathbf{W^s}$, and their particle densities $n_s$ in $\mathbf{D^s}$. We can then apply the HK theorem and define the non-interacting analogue of $F_{\rm HK}$, which is

$$T_s[n_s] \ := \ E_s\left[v_s[n_s]\right] - \int d^3r \ v_s[n_s](\mathbf{r})n_s(\mathbf{r}). \tag{2.27}$$

Restricting ourselves to non-degenerate ground states, the expression (2.27) can be re-written stressing the one-to-one correspondence among densities and wavefunctions, as follows

$$T_s[n_s] = \langle \Psi_s[n_s]|\hat{T}|\Psi_s[n_s]\rangle \ . \tag{2.28}$$

A fundamental assumption is now introduced: For each element $n$ of $\mathbf{D}$ a potential $v_s$ in $\mathbf{P^s}$ exists, such that the corresponding ground-state particle density $n_s$ equals $n$. In other words, it is assumed that the interacting v-representable densities are also non-interacting v-representable. In this way, the interacting problem is mapped onto a non-interacting one. To which extent this can be justified rigorously will be discussed in Sec. (2.4.3).

Given the existence of $v_s$, the Hohenberg-Kohn theorem (applied to the class of non-interacting systems) ensures that $v_s$ is unique up to an additive constant. As a result, we find the particle density of the interacting system by solving the eigenvalue problem

$$\hat{H}_s\Psi = E_s\Psi_s, \tag{2.29}$$

with the same boundary conditions as for the interacting system. Eq. (2.29) is usually referred as the Kohn-Sham equation. For non-degenerate ground states, the Kohn-Sham ground-state wavefunction is a single Salter determinant. In general, when considering degenerate ground states, it can be expressed as a linear combination of several Slater determinants [7, 8, 9]. The situation can be even more complex. In fact, there exist interacting ground states with particle densities that can be represented only by means of an ensemble of non-interacting particle densities [10, 11, 12, 13, 14]. We will come back to this point in Sec. (2.4.2). Here we continue by considering the simplest cases. Hence, Eq. (2.29) can be rewritten in terms of the single-particle orbitals as follows

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\varphi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}\varphi_{i\sigma}(\mathbf{r})\ . \tag{2.30}$$

Here $i$ is a collective index for all quantum numbers except spin. The single-particle orbitals $\varphi_{i\sigma}(\mathbf{r})$ are commonly called Kohn-Sham orbitals. We emphasize that – although in DFT the particle density is the only basic variable – the Kohn-Sham orbitals are proper fermionic single-particle states. The ground-state Kohn-Sham wavefunction is obtained by occupying the $N$ eigenstates with lowest eigenvalues. The corresponding density is obtained as

$$n(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}|\varphi_{i\sigma}(\mathbf{r})|^2. \tag{2.31}$$

In the next section, we consider the consequences of introducing the Kohn-Sham system in DFT.

### 2.3.1 Exchange-correlation energy functional

An important decomposition for $F_{\mathrm{HK}}[n]$ can be introduced by extracting all those terms for which an exact expression, either in terms of the Kohn-Sham orbitals or particle density, is available. This decomposition is given by

$$F_{\mathrm{HK}}[n] = T_s[n] + U[n] + E_{xc}[n]\ . \tag{2.32}$$

The first term is the kinetic energy of the Kohn-Sham system

$$T_s[n] = -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N}\int \mathrm{d}^3r\ \varphi^*_{i\sigma}(\mathbf{r})\nabla^2\varphi_{i\sigma}(\mathbf{r})\ , \tag{2.33}$$

the second contribution to the decomposition (2.32) is the Hartree energy

$$U[n] = \frac{1}{2}\int\int d^3r d^3r' \ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ , \tag{2.34}$$

and the remainder is defined as the exchange-correlation energy

$$E_{xc}[n] := F_{\mathrm{HK}}[n] - T_s[n] - U[n] \ . \tag{2.35}$$

For systems consisting of one single electron, there is no electron-electron interaction (i.e. $V_{ee} = 0$). Hence, by Eq. (2.21), the functional $F_{HK}[n]$ reduces to $T_s[n]$. Consequently, for one-particle systems, $E_{xc}[n]$ equals $-U[n]$ as an immediate implication of Eq. (2.35). For systems having more than one particle, $E_{xc}$ accounts for the exchange and correlation energy contributions. Comparing Eqs. (2.32) and (2.20), the following expression for the total energy density functional is obtained

$$E_{v,\mathrm{HK}}[n] = T_s[n] + U[n] + E_{xc}[n] + \int d^3r \ n(\mathbf{r})v(\mathbf{r}). \tag{2.36}$$

Consider now the Euler equations for the interacting and non-interacting system, i.e., the necessary condition for having the energy minimum

$$\frac{\delta F_{\mathrm{HK}}}{\delta n(\mathbf{r})} + v(\mathbf{r}) = 0 \tag{2.37}$$

and

$$\frac{\delta T_s}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) = 0, \tag{2.38}$$

respectively. Note that we have just assumed the differentiability of the functionals. This is a crucial assumption to be reconsider in Sec. (2.4.3). Making use of definition (2.32), from Eq.s (2.37) and (2.38) we obtain

$$v_s(\mathbf{r}) = v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v(\mathbf{r}). \tag{2.39}$$

Here, $v$ is the external potential acting upon the interacting electrons, $v_H$ is the Hartree potential

$$v_H(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{2.40}$$

and $v_{xc}$ is the so-called exchange-correlation potential

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \tag{2.41}$$

Summarizing, the importance of decomposition (2.32) is that a significant part of $F_{\mathrm{HK}}$ is given in the explicit form of $T_s[n] + U[n]$ without approximation. In particular, while the Hartree energy (Eq. (2.34)) has an explicit expression in terms

of the particle density, the kinetic energy of the Kohn-Sham system (Eq. (2.33)) has an explicit expression in terms of the Kohn-Sham orbitals. Still, $E_{xc}$ represents an important part of the total energy, whose exact functional form is unknown and which, therefore, has to be approximated in practice. However, good and surprisingly efficient approximations exist for $E_{xc}$.

We will discuss a particular class of approximations which are known under the name of orbital functionals in the following chapter. Before that, in the remainder of this chapter we discuss somewhat more formal aspects about the foundations of DFT and the Kohn-Sham scheme.

## 2.4 Reformulations of DFT

In this section we consider reformulations of DFT, which has the merit to analyze and solve, at least to some reasonable extent, important technical questions at the heart of DFT. Also, they influenced and still influence the analysis of the properties of the exact functionals. An extensive, careful and up-to-dated review of the topics which follow is given in Ref. [15].

### 2.4.1 Levy's formulation

An important consequence of the HK theorem is that the Rayleigh-Ritz variational principle based on the wavefunction can be replaced by a variational principle based on the particle density. Let us emphasize again that the latter is valid for all the densities in the set $\mathbf{D}$, which is the set of v-representable densities. Unfortunately, v-representability is a condition which is not easily verified for a given function $n(\mathbf{r})$. As a consequence, one might worry that in applying the Hohenberg-Kohn variational principle, there is the possibility of plugging in trial densities not contained in $\mathbf{D}$ and then obtain an unphysical minimum value. The solution of this problem was provided by Levy [16], and later reformulated and extended by Lieb [7].

First, the set $\mathbf{W}$ is enlarged to $\mathbf{W_N}$ which includes all possible antisymmetric and normalized N-particle wavefunctions $\Psi$. Note that $\mathbf{W_N}$ also contains N-particle wavefunctions which are *not* ground-state wavefunctions to some external potential $v$. Correspondingly, the set $\mathbf{D}$ is replaced by the set of N-representable densities, $\mathbf{D_N}$. This set of particle densities is generated from the wavefunctions in $\mathbf{W_N}$ by using Eq. (2.6). The densities in the set $\mathbf{D_N}$ are called N-representable, since they all come from N-particle antisymmetric wavefunctions. Note that following the explicit construction given by Harriman [17], any integrable and positive function $n(\mathbf{r})$ is N-representable.

Levy reformulated the variational principle in a constrained-search fashion, as follows

$$E_v = \inf_{n\in\mathbf{D_N}} \left\{ \inf_{\Psi\to n|\Psi\in\mathbf{W_N}} \langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle + \int d^3r\; n(\mathbf{r})v(\mathbf{r}) \right\}. \qquad (2.42)$$

In this formulation, the search inside the curly brackets is constrained to those wavefunctions which yield a given density $n$ - therefore the name "constrained search". The minimum is then found by the outer search over all densities. It is interesting to note that $v(\mathbf{r})$ acts like a Lagrangian multiplier to satisfy the constraint on the density at each point in space. Also note that $F_{\rm HK}$ is replaced by

$$F_{\rm LL}[n] := \inf_{\Psi\to n}\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle, \quad \text{with } \Psi\in\mathbf{W_N} \text{ and } n\in\mathbf{D_N}\ . \tag{2.43}$$

Furthermore it can be shown that the infimum is a minimum [7]. While the set $\mathbf{W_N}$ is convex, the functional $F_{\rm LL}[n]$ is not convex [7]. This poses serious problem in proving the differentiability of $F_{\rm LL}$. The Lieb formulation of DFT (that will be described in the next section) is, to some extent, a remedy to this limitation. Still following the work of Levy, the functional $E_{\rm HK}$ can then be replaced by

$$E_{v,\rm LL}[n] := F_{\rm LL}[n] + \int d^3r\ n(\mathbf{r})v(\mathbf{r}), \quad \text{with } n\in\mathbf{D_N}. \tag{2.44}$$

Let us also observe that if, for a given $v_0$, the corresponding ground-state particle density, $n_0$, is inserted, then

$$E_{v_0,\rm LL}[n_0] = E_{v_0,\rm HK}[n_0] = E[v_0] \tag{2.45}$$

from which

$$F_{\rm LL}[n] = F_{\rm HK}[n], \quad \text{for all } n\ \in\ \mathbf{D}\ . \tag{2.46}$$

Furthermore, if any other particle density is inserted we obtain

$$E_{v_0,\rm LL}[n] \geq E[v_0], \quad \text{for}\ \ n\neq n_0\ \ \text{and } n\in\mathbf{D_N}. \tag{2.47}$$

In this approach, the degenerate case does not require particular care. In fact, the correspondences between potentials, wavefunctions and densities are not explicitly employed as it was done in the previous Hohenberg-Kohn formulation. We may say that this is another advantage of substituting the V-representability with the N-representability condition, and of introducing the "constrained-search" of the minima. However it is important to stress that the N-representability is of secondary importance in the context of the Kohn-Sham scheme, for which still it is necessary to assume that the densities of the interacting electrons are non-interacting v-representable as well. We discuss this point in more detail in the next section, where the ensemble and Lieb formulation of DFT are introduced.

### 2.4.2 Ensemble-DFT and Lieb's formulation

Do all the densities of $\mathbf{D_N}$ come from some local external potential? The answer to this question, which has been given by Levy and Lieb [7], is negative. The

point is: The sets $\mathbf{D}$ is not convex. In fact, linear combinations of densities, $n_k(\mathbf{r})$, corresponding to degenerate ground states, $\Psi_k$,

$$n(\mathbf{r}) = \sum_{k=1}^{M} \lambda_k n_k(\mathbf{r}), \;\; \lambda_k = 1 \;\; (0 \leq \lambda_k \leq 1) \tag{2.48}$$

in general are not in $\mathbf{D}$ [7, 18]. These particle densities are densities of ensembles, defined through the (statistical, or von Neuman) density operator

$$\hat{D} = \sum_{k=1}^{M} \lambda_k |\Psi_k\rangle\langle\Psi_k|, \quad \text{with } \sum_{k=1}^{M} \lambda_k = 1 \;\; (0 \leq \lambda_k \leq 1) \; . \tag{2.49}$$

.

Expectation values of an operator $\hat{O}$ on ensembles are defined as

$$O := \mathrm{Tr}\left\{\hat{D}\hat{O}\right\}, \tag{2.50}$$

where the symbol "Tr" stands for the trace taken over an arbitrary complete set of orthonormal N-particle states

$$\mathrm{Tr}(\hat{D}\hat{O}) := \sum_k \langle\Phi_k|(\hat{D}\hat{O})|\Phi_k\rangle. \tag{2.51}$$

The trace is invariant under unitary transformations of the complete set, and we can choose it as formed by the eigenstates of the Hamiltonian $\hat{H}$ which includes the ground states in Eq.(2.49). As a result

$$\mathrm{Tr}\left\{\hat{D}\hat{O}\right\} = \sum_{k=1}^{M} \lambda_k \langle\Psi_k|\hat{O}|\Psi_k\rangle. \tag{2.52}$$

Clearly, the energy obtained from a density matrix of the form (2.49) equals the ground state total energy of the system under consideration.

Particle-densities of the form (2.48) are called ensemble v-representable densities, shortly E-V-densities. We denote this set of densities as $\mathbf{D_{EV}}$. Densities that can be obtained from a single ground state are said to be pure-state (PS) v-representable, or shortly PS-V-densities. The functional $F_{\mathrm{HK}}$ can then be extended as [19]

$$F_{\mathrm{EHK}}[n] := Tr\left\{\hat{D}\left(\hat{T} + \hat{V}_{ee}\right)\right\}, \quad \text{with } n \in \mathbf{D_{EV}} \tag{2.53}$$

where $\hat{D}$ of the form (2.49) is any density matrix giving the density $n$. However the set $\mathbf{D_{EV}}$, just like $\mathbf{D}$, is difficult to characterize. Moreover, as for $F_{\mathrm{HK}}$ and $F_{\mathrm{LL}}$, also for $F_{\mathrm{EHK}}$ (and for the non-interacting versions of the same functionals), a proof of their differentiability is not available. But in the so-called Lieb formulation the

differentiability question can be addressed [7, 8, 9]. In this formulation, the universal functional is defined as

$$F_{\rm L}[n] := \inf_{\hat{D}\to n} Tr\left\{\hat{D}\left(\hat{T}+\hat{V}_{ee}\right)\right\}, \quad \text{with } n \in \mathbf{D_N}; \tag{2.54}$$

and it can be shown that the infimum is a minimum [7]. Note that in definition (2.54), $\hat{D}$ is a generic density matrix of the form

$$\hat{D} = \sum_k \lambda_k |\Psi_k\rangle\langle\Psi_k|, \quad \text{with } \sum_k \lambda_k = 1 \;\; (0 \le \lambda_k \le 1) \;, \tag{2.55}$$

where $\Psi_k \in \mathbf{W_N}$, and the sum is not restricted to a finite number of degenerate ground states as in Eq. (2.49). Clearly

$$F_{\rm L}[n] \le F_{\rm LL}[n], \quad \text{for } n \in \mathbf{D_N}, \tag{2.56}$$

and

$$F_{\rm L}[n] = F_{\rm LL}[n] = F_{\rm HK}[n], \quad \text{for } n \in \mathbf{D} \;. \tag{2.57}$$

$F_{\rm L}[n]$ is defined on a convex set, and it is a convex functional. Hence, it is possible to establish to show that $F_{\rm L}[n]$ is differentiable at any ensemble v-representable densities and nowhere else (the differentiability is meant in the Gateaux sense) [7]. Thus, in minimizing the functional

$$E_{\rm L}[n] := F_{\rm L}[n] + \int d^3r \; n(\mathbf{r})v(\mathbf{r}) \;. \tag{2.58}$$

with respect elements of $\mathbf{D_{EV}}$ by the Euler-Langrange equation

$$\frac{\delta F_{\rm L}}{\delta n(\mathbf{r})} + v(\mathbf{r}) = 0 \tag{2.59}$$

is well defined on the set $\mathbf{D_{EV}}$. As the Euler-Lagrange equation is well-defined for these densities, they are found as the solution of the same equation.

### 2.4.3 Kohn-Sham scheme on rigorous ground

We can finally address, although briefly, some important points about the Kohn-Sham scheme and its rigorous justification. The results for $F_{\rm L}$, given in the previous section, carry over to $T_{\rm L}[n]$. That is, the functional

$$T_{\rm L}[n] = \inf_{\hat{D}\to n} Tr\left\{\hat{D}\hat{T}\right\}, \quad \text{with } n \in \mathbf{D_N} \tag{2.60}$$

is differentiable at any non-interacting ensemble v-representable densities, and nowhere else. We may imagine to gather all these densities in the set $\mathbf{D^s_{EV}}$. It is then clear that the Euler-Langrange equation

$$\frac{\delta T_{\rm L}}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) = 0 \tag{2.61}$$

is well defined on the set $\mathbf{D}^{\mathbf{s}}_{\mathbf{EV}}$ only. One can then redefine the exchange-correlation functional as

$$E_{xc,\mathrm{L}}[n] = F_{\mathrm{L}}[n] - T_{\mathrm{L}}[n] - U[n], \tag{2.62}$$

and observe that the differentiability of $F_{\mathrm{L}}[n]$ and $T_{\mathrm{L}}[n]$ implies the differentiability of $E_{xc}[n]$ only on $\mathbf{D}_{\mathbf{EV}} \cap \mathbf{D}^{\mathbf{s}}_{\mathbf{EV}}$. Remain the question how large the latter set is. For densities defined on a discrete lattice (finite or infinite) it is known [20] that $\mathbf{D}_{\mathbf{EV}} = \mathbf{D}^{\mathbf{s}}_{\mathbf{EV}}$. Moreover, in the continuum limit, $\mathbf{D}_{\mathbf{E}}$ and $\mathbf{D}^{\mathbf{s}}_{\mathbf{E}}$ can be shown to be dense with respect to each other [7, 8, 9]. This implies that any element of $\mathbf{D}_{\mathbf{EV}}$ can be approximated, with an arbitrary accuracy, by means of an element of $\mathbf{D}^{\mathbf{s}}_{\mathbf{EV}}$. These statements basically cover all situations of physical interest.

At last, we point out that theoretical indications and numerical examples of interacting PS-V-densities which are non-interacting E-V-densities but not non-interacting PS-V-densities have been given [10, 11, 12, 13]. This fact well justifies not only the theoretical need but also the practical importance of the Lieb formulation: in which the Kohn-Sham scheme is both flexible enough and mathematically well justified.

# Chapter 3

# Orbital functionals

The success of DFT is largely due to the availability of increasingly accurate approximations to the exchange-correlation energy functional. While the simple local density approximation (LDA) proved to be surprisingly accurate especially in solid state physics, only the advent of the so-called generalized gradient approximations (GGA's) with their increased accuracy led to an explosion of applications of DFT in quantum chemistry. The development of new, improved functionals is an ongoing effort. In this thesis, we are mainly interested in explicit functionals of the Kohn-Sham orbitals, rather than explicit functionals of the density (such as LDA or GGA). Since the density, by virtue of the Hohenberg-Kohn theorem, determines the potential, and the potential determines the orbitals, such orbital functionals are sometimes called *implicit* density functionals. Here we review how it is possible to make use of such approximations [21, 22], and for sake of simplicity we will limit our considerations to non degenerate states. Extensions of the present basic formulation to deal with non-collinear magnetization, currents and the corresponding conjugate fields are among the main topics of the present work, and are reported in chapter 5.

## 3.1 Introduction

The idea of using implicit density functionals was already introduced in the original Kohn-Sham formalism. In fact, the kinetic energy density functional $T_s[n]$ is expressed, without approximation, in terms of the Kohn-Sham orbitals, i.e.,

$$T_s[n] = -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\int \mathrm{d}^3r\ \varphi^*_{i\sigma}(\mathbf{r})\nabla^2\varphi_{i\sigma}(\mathbf{r})\ . \tag{3.1}$$

and thus the dependence on the density $n$ is implicitly carried by the orbitals.

Another important example of an orbital functional is the exact-exchange (EXX) energy functional

$$E_x^{\mathrm{EXX}}[n] := -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{j,k=1}^{N_\sigma}\int \mathrm{d}^3r\int \mathrm{d}^3r'\frac{\varphi^*_{j\sigma}(\mathbf{r})\varphi^*_{k\sigma}(\mathbf{r}')\varphi_{j\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{3.2}$$

The correlation energy is then defined as

$$E_c[n] := E_{xc}[n] - E_x[n] \; . \tag{3.3}$$

Note that definition (3.2) is valid only when the Kohn-Sham ground states can be expressed as a single Slater determinant, such as in the case of non-degenerate ground states.

In expression (3.2), we recognize the Fock term of the HF approach. But, it is very important to distinguish the HF method and the EXX approximation. While the HF wavefunction is meant to provide an approximation for the many-body wavefunction itself, the Kohn-Sham wavefunction is meant to reproduce the exact particle density. Another difference is that, while the Hartree-Fock orbitals are produced by a non-local effective potential, the Kohn-Sham orbitals are produced by a single particle equation with a local effective potential.

An important property of EXX is that it is free of self-interaction: this means that the orbital does not "feel" the electrostatic potential formally created by itself as part of the Hartree potential because this term is exactly cancelled by a corresponding term in the exchange potential. The EXX potential decays asymptotically as $-1/r$ for finite systems and this asymptotic form acts on *all* the orbitals. Therefore, the KS potential in EXX approximation supports a whole Rydberg series of unoccupied bound states as well as negative ions. By contrast, the HF approximation does not support the Rydberg series.

Unlike the EXX functional, explicit density functionals like LDA or GGA typically are not free of self-interaction. One of the consequences is the incorrect exponential asymptotic decay of the corresponding exchange-correlation potentials for finite systems. Some time ago, Perdew and Zunger [23] proposed to make any approximate $E_{xc}^{approx}$ self-interaction free by removing the self-interaction explicitly for each orbital. As a result an expression depending explicitly on the Kohn-Sham orbitals is obtained.

Another advantage of orbital dependent functionals over standard explicit density functionals like LDA or GGA is that they also can reproduce the derivative discontinuity $\Delta_{xc}$ of the exchange correlation functional as a function of particle number which occurs at integer particle number $N$ [24, 25, 26]. This discontinuity enters the expression for the so-called fundamental energy gap of periodic solids which is the analogue of the so-called chemical hardness of finite species.

Two other classes of orbital functionals are also discussed in the literature. One of them are the so-called hybrid functionals which are constructed by approximating the exchange energy by a *fraction* of exact exchange plus some GGA part for the remainder. Hybrids have been introduced in quantum chemistry [27, 28, 29, 30] and have been found to yield accurate results for many energetic properties.

The second class of functionals we would like to mention here are the so-called meta-GGA's [31, 32, 33] which are of the general form

$$E_{xc}^{\mathrm{MGGA}}[n] = \int \mathrm{d}^3 r \; g(n, \nabla n, \tau) \tag{3.4}$$

where

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N} |\nabla \varphi_{i\sigma}(\mathbf{r})|^2 \tag{3.5}$$

is the kinetic energy density associated with the Kohn-Sham orbitals. It is through their dependence on $\tau$, that meta-GGA's also become orbital functionals.

Orbital functionals constitute a natural framework for the systematic construction of approximations for the exchange-correlation functional in the spirit of perturbation theory. Görling and Levy [34] have suggested a perturbative expansion of the exchange-correlation energy functional in powers of $e^2$,

$$E_{xc} = \sum_{j=1}^{\infty} e^{2j} E_{xc}^{(j)} = e^2 E_x^{\mathrm{EXX}} + e^4 E_c^{(2)} + \ldots \tag{3.6}$$

where we have used that

$$E_{xc}^{(1)} = E_x^{EXX}. \tag{3.7}$$

Expression (3.6) implies that also $v_{xc}$ can be written as a power series in $e^2$,

$$v_{xc}(\mathbf{r}) = \sum_{j=1}^{\infty} e^{2j} v_{xc}^{(j)}(\mathbf{r}) = e^2 v_x^{\mathrm{EXX}}(\mathbf{r}) + e^4 v_c^{(2)}(\mathbf{r}) + \ldots \tag{3.8}$$

where the first order term is the EXX potential.

One of the interesting properties of orbital-dependent correlation energy functionals is their ability to properly describe long-range van-der-Waals interactions for well-separated subsystems. Engel et. al. [35] have mapped out the binding energy curve of rare gas dimers as a function of atomic separation using the second order functional $E_c^{(2)}$. They found a qualitatively correct description, however, a full quantitative description apparently requires higher-order correlations to be taken into account.

Yet another representation of $E_{xc}$ is related to the dynamic linear density response function of the interacting system of interest. The derivation of this representation requires ideas from time-dependent density functional theory (TDDFT). For the fundamental ideas underlying TDDFT, the interested reader is referred to the review of Refs. [36, 37].

## 3.2 Optimized effective potential

Once we accept to use an expression for $E_{xc}$ which explicitly depends on the Kohn-Sham orbitals, the main question is how to compute the corresponding exchange-correlation potential of Eq. (2.41).

The way to accomplish this task is indicated by the Hohenberg-Kohn theorem. Application of this theorem to non-interacting systems shows that there is a one-to-one correspondence between $n(\mathbf{r})$ and $v_s(\mathbf{r})$. The latter, in turn, determines the

Kohn-Sham orbitals which yield the density we started from. Thus, we can formally write any of these quantities as functional of one of the other quantities, and an explicit dependence on one of them introduces an implicit dependence on the others. It is then clear that a variation of the particle density corresponds to a variation of the Kohn-Sham potential which, in turn, induces a variation of (all) the orbitals. We can use this observation in order to rewrite Eq. (2.41) using the chain rule of functional differentiation as follows

$$v_{xc}(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \mathrm{d}^3 r' \left[ \frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta n(\mathbf{r})} + c.c. \right] . \tag{3.9}$$

In writing the latter equation, we have tacitly restricted the exchange-correlation functional to depend on the occupied Kohn-Sham orbitals only. Now, let us observe that the functional derivative of $E_{xc}$ with respect to the orbitals can be easily calculated given its explicit functional form in terms of the orbitals. However, as we have observed above, the dependence of the orbitals on the particle density is not explicit. Hence, to calculate the functional derivative of the orbitals with respect to the density, we can view the orbitals as functionals of $v_s(\mathbf{r})$, yielding

$$v_{xc}(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \mathrm{d}^3 r' \int \mathrm{d}^3 r'' \left[ \frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r}'')} \frac{\delta v_s(\mathbf{r}'')}{\delta n(\mathbf{r})} + c.c. \right] . \tag{3.10}$$

The third functional derivative on the right-hand side of this equation may now be identified as the inverse of the static density response function of the Kohn-Sham system defined by

$$\chi_s(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} . \tag{3.11}$$

Operating with $\chi_s$ on Eq. (3.10) from the right, one obtains

$$\int \mathrm{d}^3 r' v_{xc}(\mathbf{r}') \chi_s(\mathbf{r}', \mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \mathrm{d}^3 r' \left[ \frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \right] . \tag{3.12}$$

Now all the terms in this equation can be expressed in terms of the Kohn-Sham orbitals and eigenvalues. The functional derivative of the orbitals with respect to the potential can be obtained exactly from first order perturbation theory and reads

$$\frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r})} = G_{s,j\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \tag{3.13}$$

where we have defined the (projected) Green's function of the Kohn-Sham system as

$$G_{s,j\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{\substack{k \\ k \neq j}} \frac{\varphi_{k\sigma}(\mathbf{r}) \varphi^*_{k\sigma}(\mathbf{r}')}{\varepsilon_{j\sigma} - \varepsilon_{k\sigma}} . \tag{3.14}$$

For simplicity, we have assumed here that the single particle levels are non-degenerate. The static linear density response function of the Kohn-Sham system may be written as

$$\chi_s(\mathbf{r},\mathbf{r}') = \sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma}\left[\varphi^*_{j\sigma}(\mathbf{r})G_{s,j\sigma}(\mathbf{r},\mathbf{r}')\varphi_{j\sigma}(\mathbf{r}') + c.c.\right] . \tag{3.15}$$

Substituting (3.13) and (3.15) into (3.12) yields

$$\sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma}\int \mathrm{d}^3r' \left\{\varphi^*_{j\sigma}(\mathbf{r}')\big[v_{xc}(\mathbf{r}') - u_{xc,j\sigma}(\mathbf{r}')\big]G_{s,j\sigma}(\mathbf{r}',\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) + c.c.\right\} = 0 \tag{3.16}$$

where we have defined

$$u_{xc,j\sigma}(\mathbf{r}') := \frac{1}{\varphi^*_{j\sigma}(\mathbf{r}')}\frac{\delta E_{xc}}{\delta\varphi_{j\sigma}(\mathbf{r}')} . \tag{3.17}$$

Introducing the so-called orbital shifts [38, 39, 40]

$$\psi^*_{j\sigma}(\mathbf{r}) := \int \mathrm{d}^3r'\varphi^*_{j\sigma}(\mathbf{r}')\big[v_{xc}(\mathbf{r}') - u_{xc,j\sigma}(\mathbf{r}')\big]G_{s,j\sigma}(\mathbf{r}',\mathbf{r}) \tag{3.18}$$

allows us to rewrite Eq. (3.16) in a very compact way,

$$\sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma}\left[\psi^*_{j\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) + c.c.\right] = 0 , \tag{3.19}$$

which is the standard form of the so called optimized effective potential (OEP) equation. The name of this equation suggests that the resulting potential is *optimal*, but in which sense is it so?

In DFT, the value of the ground state energy corresponds to the minimum value of the density functional for the total energy. This minimum is obtained only if the exact ground-state particle density is inserted. Now the idea of the Kohn-Sham method is to calculate that density from single-particle orbitals solving a single-particle Schrödinger equation. Hence, in order to produce those single-particle orbitals we need to use the proper single-particle potential: namely the one which is optimized in the sense that its orbitals minimize the total-energy functional. This is nothing but the Kohn-Sham potential [41, 42]. In fact, for the argument given above, the total energy density functional, Eq. (2.36), can be thought to implicitly depend on the effective potential through the particle density. Using again the chain rule, one obtains

$$\frac{\delta E_v[n]}{\delta v_s(\mathbf{r})} = \int \mathrm{d}^3r' \frac{\delta E_v}{\delta n(\mathbf{r}')}\frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} = 0 , \tag{3.20}$$

where the last equality follows from the Hohenberg-Kohn variational principle. This point of view provides another derivation of the OEP equation. To this end, we just

need to substitute the dependence on the particle density with the dependence on the orbitals. Then, Eq. (3.20) may be written as

$$\frac{\delta E_v[n]}{\delta v_s(\mathbf{r})} = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \mathrm{d}^3 r' \left[ \frac{\delta E_v}{\delta \varphi^*_{j\sigma}(\mathbf{r})} \frac{\delta \varphi^*_{j\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \right] = 0. \tag{3.21}$$

The functional derivative of $E_v$ with respect to the Kohn-Sham orbitals is easily expressed as

$$\frac{\delta E_v}{\delta \varphi^*_{j\sigma}(\mathbf{r})} = \left[ -\frac{\nabla^2}{2} + v(\mathbf{r}) + v_H(\mathbf{r}) \right] \varphi_{j\sigma}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \varphi^*_{j\sigma}(\mathbf{r}')} \tag{3.22}$$

which, by using the Kohn-Sham equation, may be expressed as

$$\frac{\delta E_v}{\delta \varphi^*_{j\sigma}(\mathbf{r})} = \left[ \varepsilon_{j\sigma} - v_{xc}(\mathbf{r}) \right] \varphi_{j\sigma}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \varphi^*_{j\sigma}(\mathbf{r}')} \, . \tag{3.23}$$

Inserting this expression into Eq. (3.21) and using the orthonormality of the Kohn-Sham orbitals, one finally arrives at the integral equation (3.16) for $v_{xc}(\mathbf{r})$. In other words, the optimized effective potential is that *local* potential that yields single-particle orbitals which minimize the total energy [43, 44].

## 3.3 KLI and CEDA approximation

The OEP equation (3.16) is an integral equation to be solved for the exchange-correlation potential $v_{xc}(\mathbf{r})$. Historically, this solution first has been achieved for systems with very high symmetry [44]. In order to reduce the computational effort, simplifying, yet accurate, approximations to the full OEP equations have been suggested which will be discussed in this section.

We see that an important ingredient of the OEP equation is the Green's function of Eq. (3.14) which involves a summation over occupied and unoccupied Kohn-Sham orbitals. Sharp and Horton [43] and later Krieger, Li, and Iafrate (KLI) [45, 46] proposed to approximate the Green's function (3.14) by replacing the energy denominators by a constant value, $\Delta$, independent of the particle indices $j$ and $k$. Using the completeness of the Kohn-Sham orbitals, this approximation leads to

$$\begin{aligned} G^{\mathrm{KLI}}_{s,j\sigma}(\mathbf{r},\mathbf{r}') &= \frac{1}{\Delta} \Big[ \sum_{k=1}^{\infty} \varphi^*_{k\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}') - \varphi^*_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}') \Big] \\ &= \frac{1}{\Delta} \Big[ \delta(\mathbf{r}-\mathbf{r}') - \varphi^*_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}') \Big] \, . \end{aligned} \tag{3.24}$$

Substitution into Eq. (3.18) gives

$$\sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} n_{j\sigma}(\mathbf{r}) \left[ v^{\mathrm{KLI}}_{xc}(\mathbf{r}) - u_{xc,j\sigma}(\mathbf{r}) - \left( \overline{v}^{KLI}_{xc,j\sigma} - \overline{u}_{xc,j\sigma} \right) \right] + c.c. = 0 \, , \tag{3.25}$$

where we have used the definitions

$$n_{j\sigma}(\mathbf{r}) := \varphi^*_{j\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}), \tag{3.26}$$

and the constants

$$\overline{v}^{\rm KLI}_{xc,j\sigma} := \int \mathrm{d}^3r\ \varphi^*_{j\sigma}(\mathbf{r}) v^{\rm KLI}_{xc}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r})\ . \tag{3.27}$$

The constants $\overline{u}_{xc,j\sigma}$ are defined in an analogous way as orbital averages of $u_{xc,j\sigma}(\mathbf{r})$ with respect to the orbital $\varphi_{j\sigma}$. Solving Eq. (3.25) for $v^{\rm KLI}_{xc}(\mathbf{r})$ yields

$$v^{\rm KLI}_{xc}(\mathbf{r}) = \frac{1}{2n(\mathbf{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} n_{j\sigma}(\mathbf{r}) \left( u_{xc,j\sigma}(\mathbf{r}) + \overline{v}^{\rm KLI}_{xc,j\sigma} - \overline{u}_{xc,j\sigma} + c.c. \right)\ . \tag{3.28}$$

This so-called KLI equation has transformed the OEP integral equation into a linear algebraic equation in which one needs to deal with the $N = N_\uparrow + N_\downarrow$ occupied orbitals. Since one does not need to consider the infinitely many unoccupied orbitals, the KLI equation is much easier than the OEP equation in practical applications. Although this transformation is approximate, in many cases the deviations from full OEP results are small.

As we have seen, in the KLI approximation the Kohn-Sham orbital energy differences $\varepsilon_{j\sigma} - \varepsilon_{k\sigma}$ are approximated by one and the same constant, irrespective of the sign of different terms. In a similar spirit, a different approximation known as common energy denominator approximation (CEDA) [47] or localized Hartree-Fock (LHF) [48] approximation has been proposed which only replaces the energy differences for occupied-unoccupied orbital pairs by a constant while it retains the energy differences for the occupied-occupied pairs. For the Green's function this gives

$$G^{\rm CEDA}_{s,j\sigma}(\mathbf{r},\mathbf{r}') = \sum_{\substack{k=1\\k\neq j}}^{N_\sigma} \frac{\varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_j - \varepsilon_k} + \frac{1}{\Delta} \sum_{k>N_\sigma} \varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')\ . \tag{3.29}$$

Adding and substracting the contribution of the occupied orbitals with the common energy denominator and using the completeness of the Kohn-Sham orbitals yields

$$G^{\rm CEDA}_{s,j\sigma}(\mathbf{r},\mathbf{r}') = \frac{\delta(\mathbf{r}-\mathbf{r}')}{\Delta} + \sum_{\substack{k=1\\k\neq j}}^{N_\sigma} \frac{\varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_j - \varepsilon_k} - \frac{1}{\Delta} \sum_{k=1}^{N_\sigma} \varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')\ , \tag{3.30}$$

which, when inserted into Eq. (3.16), leads to the following equation for the exchange-correlation potential in the CEDA approximation

$$\begin{aligned} v^{\rm CEDA}_{xc}(\mathbf{r}) \ &= \ \frac{1}{2n(\mathbf{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \Big[ n_{j\sigma}(\mathbf{r}) u_{xc,j\sigma}(\mathbf{r}) \\ &\quad + \sum_{i=1}^{N_\sigma} \varphi^*_{i\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) \left( \overline{v}^{\rm CEDA}_{xc,ji\sigma} - \overline{u}_{xc,ji\sigma} \right) + c.c. \Big] \end{aligned} \tag{3.31}$$

with

$$\overline{v}_{xc,ji\sigma}^{\mathrm{CEDA}} := \int \mathrm{d}^3 r \varphi_{j\sigma}^*(\mathbf{r}) v_{xc}^{\mathrm{CEDA}}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \tag{3.32}$$

and similarly for $\overline{u}_{xc,ji\sigma}$. One immediately sees that the CEDA reduces to the KLI approximation if all off-diagonal terms $i \neq j$ in the second sum are neglected.

Both the KLI as well as the CEDA approximation (Eqs. (3.28) and (3.31), respectively) can easily be implemented within a self-consistent scheme with essentially the same effort. From a theoretical point of view, CEDA has the advantage of being invariant under unitary transformations of the occupied orbitals while KLI is not. From a practical point of view, it turns out that CEDA and KLI results are often very similar.

## 3.4 Exact transformation of the OEP equation

In this section we discuss a way to transform the OEP equations exactly which, on one hand, highlights the role of the orbital shifts (3.18) and, on the other hand, allows us to motivate the KLI approximation from a different perspective. We start by noting that the non-interacting Green's function satisfies the following differential equation

$$\left(\hat{h}_s(\mathbf{r}) - \varepsilon_{j\sigma}\right) G_{s,j\sigma}(\mathbf{r}', \mathbf{r}) = -\left(\delta(\mathbf{r} - \mathbf{r}') - \varphi_{j\sigma}^*(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')\right) \ , \tag{3.33}$$

where $\hat{h}_s(\mathbf{r})$ is the Kohn-Sham Hamiltonian. Acting with the operator $(\hat{h}_s(\mathbf{r}) - \varepsilon_{j\sigma})$ on Eq. (3.18) yields a differential equation which uniquely determines [38] the orbital shifts

$$\left(\hat{h}_s(\mathbf{r}) - \varepsilon_{j\sigma}\right) \psi_{j\sigma}^*(\mathbf{r}) = -\left(v_{xc}(\mathbf{r}) - u_{xc,j\sigma}(\mathbf{r}) - (\overline{v}_{xc,j\sigma} - \overline{u}_{xc,j\sigma})\right) \varphi_{j\sigma}^*(\mathbf{r}) \ . \tag{3.34}$$

Solving for $v_s(\mathbf{r})\psi_{j\sigma}^*(\mathbf{r})$ gives

$$\begin{aligned} v_s(\mathbf{r})\psi_{j\sigma}^*(\mathbf{r}) &= -\left(v_{xc}(\mathbf{r}) - u_{xc,j\sigma}(\mathbf{r}) - (\overline{v}_{xc,j\sigma} - \overline{u}_{xc,j\sigma})\right) \varphi_{j\sigma}^*(\mathbf{r}) \\ &\quad + \left(\frac{\nabla^2}{2} + \varepsilon_{j\sigma}\right) \psi_{j\sigma}^*(\mathbf{r}) \ . \end{aligned} \tag{3.35}$$

Multiplication of this equation with $\varphi_{j\sigma}$, subsequent summation over all occupied orbitals and using the OEP equation in the form (3.19) eventually leads to

$$\begin{aligned} v_{xc}(\mathbf{r}) &= \frac{1}{2n(\mathbf{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \Bigg\{ n_{j\sigma}(\mathbf{r}) \left(u_{xc,j\sigma}(\mathbf{r}) + \overline{v}_{xc,j\sigma} - \overline{u}_{xc,j\sigma}\right) \\ &\quad + \left(\frac{\nabla^2}{2}\psi_{j\sigma}^*(\mathbf{r}) + \varepsilon_{j\sigma}\psi_{j\sigma}^*(\mathbf{r})\right) \varphi_{j\sigma}(\mathbf{r}) + c.c. \Bigg\} \ . \end{aligned} \tag{3.36}$$

The second term in the curled brackets can be rewritten by using the Kohn-Sham equations and the OEP equation again which finally leads to an exact reformulation of the OEP equation as

$$\begin{aligned} v_{xc}(\mathbf{r}) &= \frac{1}{2n(\mathbf{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \Bigg\{ n_{j\sigma}(\mathbf{r}) \left( u_{xc,j\sigma}(\mathbf{r}) + \overline{v}_{xc,j\sigma} - \overline{u}_{xc,j\sigma} \right) \\ &\quad - \nabla \cdot \left( \psi^*_{j\sigma}(\mathbf{r}) \nabla \varphi_{j\sigma}(\mathbf{r}) \right) + c.c. \Bigg\} . \end{aligned} \tag{3.37}$$

If the term involving the orbital shifts $\psi^*_{j\sigma}(\mathbf{r})$ is neglected in this expression, one again obtains the KLI potential of Eq. (3.28).

The orbital shifts $\psi_{j\sigma}(\mathbf{r})$ also play a central role in an iterative scheme to the solution of the full OEP equation recently suggested by Kümmel and Perdew [39, 40]. The idea of this scheme is to solve Eq. (3.34) for the orbital shifts directly in the following way: for a given approximate solution $v_{xc}(\mathbf{r})$ to the OEP equation, compute the right hand side of Eq. (3.34) and then solve this equation for the orbital shift $\psi_{j\sigma}(\mathbf{r})$ subject to the orthogonality constraint

$$\int \mathrm{d}^3 r \; \psi^*_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) = 0 \tag{3.38}$$

which follows from the definition (3.18) by the orthonormality of the Kohn-Sham orbitals. With the resulting orbital shifts compute the quantity

$$S(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \psi^*_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) + c.c. \tag{3.39}$$

and then compute a new potential by

$$v_{xc}^{\mathrm{new}}(\mathbf{r}) = v_{xc}^{\mathrm{old}}(\mathbf{r}) - \alpha S(\mathbf{r}) \tag{3.40}$$

with some constant $\alpha$. With this new $v_{xc}$, recompute the right hand side of Eq. (3.34) and then solve again for a new orbital shift. This is iterated a few times for fixed $\varphi_{j\sigma}$, $\hat{h}_s$ and $\varepsilon_{j\sigma}$ before eventually these quantities are also recomputed during the regular Kohn-Sham self-consistency cycle. This scheme has been applied successfully [39, 40] to compute the OEP potential (in the exact exchange approximation) not only for highly symmetric systems such as atoms but also for small sodium clusters where the direct solution of the OEP equation is a much more difficult task.

# Chapter 4

# Magnetization and current density in DFT

The generalizations of DFT designed to deal with magnetic properties of the ground states of many-electron systems are introduced in this chapter. A finite current and/or spin magnetization can either be induced by external fields, or they can occur spontaneously, e.g. in degenerate ground states of atoms, or in extended ferromagnets. Following the historical development, we first introduce spin-density-functional theory (SDFT), then we consider current-density-functional theory (CDFT). These two are then combined in the complete formulation of current-spin-density-functional theory (CSDFT). In this way, the similarities and differences of all these approaches are clarified. For the sake of simplicity, the Kohn-Sham equations are written for pure-states, which are restricted to be of the form of a single Slater determinants. Moreover, we will not specify whether the functionals are being defined in the Hohenberg-Kohn sense, or by the constrained-search procedure. In this respect, for each new version of DFT one can extend the analysis already carried out in detail in chaper 2. A special feature of SDFT and C(S)DFT not present in ordinary DFT, the so-called nonuniqueness problem, will be carefully reviewed toward the end of this chapter. The so-called $\mathbf{j}_m$-formulation of CSDFT is briefly reviewed.

## 4.1 Spin-density-functional theory

Spin density functional theory (SDFT) stems from a Hamiltonian for interacting electrons which includes a Zeeman coupling of the spin degrees of freedom to an external magnetic field $\mathbf{B}(\mathbf{r})$. The Hamiltonian reads (atomic units are used throughout)

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \int \mathrm{d}^3 r \; \hat{n}(\mathbf{r}) v(\mathbf{r}) - \int \mathrm{d}^3 r \; \hat{\mathbf{m}}(\mathbf{r}) \mathbf{B}(\mathbf{r}), \tag{4.1}$$

where

$$\hat{n}(\mathbf{r}) = \hat{\Psi}^\dagger(\mathbf{r}) \hat{\Psi}(\mathbf{r}) \; , \tag{4.2}$$

and

$$\hat{\mathbf{m}}(\mathbf{r}) = -\mu_B \hat{\Psi}^\dagger(\mathbf{r}) \boldsymbol{\sigma} \hat{\Psi}(\mathbf{r}) \tag{4.3}$$

are the particle and magnetization density operators, respectively. In the above expressions, $\boldsymbol{\sigma}$ is the vector of Pauli matrices, $\mu_B$ is the Bohr magneton, and $\hat{\Psi}^\dagger$ is the field operator defined for two-component spinor field operator

$$\hat{\Psi}^\dagger(\mathbf{r}) = (\hat{\psi}^\dagger_\uparrow(\mathbf{r}), \hat{\psi}^\dagger_\downarrow(\mathbf{r})). \tag{4.4}$$

In order to "density functionalize" the ground-state problem, the presence of the field $\mathbf{B}$ requires the use of an additional basic density. This is the magnetization density $\mathbf{m}$. Thus, the energy variational principle can be formulated as [49]

$$E_{v,\mathbf{B}} = \min_{n,\mathbf{m}} E_{v,\mathbf{B}}[n, \mathbf{m}], \tag{4.5}$$

with

$$E_{v,\mathbf{B}}[n, \mathbf{m}] = F[n, \mathbf{m}] + \int \mathrm{d}^3 r \; v(\mathbf{r}) n(\mathbf{r}) - \int \mathrm{d}^3 r \; \mathbf{m}(\mathbf{r}) \mathbf{B}(\mathbf{r}) \; . \tag{4.6}$$

As in DFT, the kinetic energy and the electron-electron interaction are taken into account through the functional $F[n, \mathbf{m}]$. Again, it is important to note that $F[n, \mathbf{m}]$ is universal in the sense that it does not depend on the external fields.

At this point, a Kohn-Sham scheme for SDFT may be introduced by assuming non-interacting ($v$,$\mathbf{B}$)-representability of the interacting densities $(n, \mathbf{m})$. In other words, it is assumed that for any interacting ground state, a non-interacting system exists having the same ground state particle and magnetization density as the interacting one. Then $F[n, \mathbf{m}]$ can be decomposed as

$$F[n, \mathbf{m}] = T_s[n, \mathbf{m}] + U[n] + E_{xc}[n, \mathbf{m}] \; , \tag{4.7}$$

where $T_s[n, \mathbf{m}]$ is the kinetic energy functional for non-interacting electrons, $U[n]$ is the classical electrostatic energy (Eq. (2.34)), and the remainder is the exchange-correlation energy functional, $E_{xc}[n, \mathbf{m}]$, as defined in SDFT. The single-particle Kohn-Sham equation of SDFT reads [49]

$$\left[ -\frac{1}{2} \nabla^2 + v_s(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \mathbf{B}_s(\mathbf{r}) \right] \Phi_i(\mathbf{r}) = \epsilon_i \Phi_i(\mathbf{r}) \; , \tag{4.8}$$

where $\Phi_i(\mathbf{r})$ are two-component, single-particle Pauli spinors. The above equation has the form of a Pauli equation, which includes only the Zeeman coupling of the effective magnetic field $\mathbf{B}_s$ to the electronic spin.

In summary, the minimization of the energy funtional (4.6) is translated into the calculation of the ground state for the Kohn-Sham system (4.8). The particle and magnetization densities are then obtained by

$$n(\mathbf{r}) = \sum_{i=1}^{N} \Phi_i^\dagger(\mathbf{r}) \Phi_i(\mathbf{r}) \; , \tag{4.9}$$

and

$$\mathbf{m}(\mathbf{r}) = -\mu_B \sum_{i=1}^{N} \Phi_i^\dagger(\mathbf{r}) \boldsymbol{\sigma} \Phi_i(\mathbf{r}) \,, \tag{4.10}$$

where the sums run over the N Kohn-Sham spinor-orbitals with lowest eigenenergies. Using the minimum condition of Eq. (4.5), for both the interacting and non-interacting system, the effective potentials can be expressed as

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \,, \tag{4.11}$$

and

$$\mathbf{B}_s(\mathbf{r}) = \mathbf{B}(\mathbf{r}) + \mathbf{B}_{xc}(\mathbf{r}) \,, \tag{4.12}$$

where the Hartree potential $v_H(\mathbf{r})$ is given by Eq.(2.40). The exchange-correlation potentials are functional derivatives of the exchange-correlation energy $E_{xc}$ with respect to the corresponding conjugate densities

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n, \mathbf{m}]}{\delta n(\mathbf{r})}\Big|_{\mathbf{m}} \tag{4.13}$$

and

$$\mathbf{B}_{xc}(\mathbf{r}) = -\frac{\delta E_{xc}[n, \mathbf{m}]}{\delta \mathbf{m}(\mathbf{r})}\Big|_{n} \,. \tag{4.14}$$

### 4.1.1 Spin-unrestricted and restricted KS scheme

SDFT is often used within the collinear approximation which assumes that the external and exchange-correlation magnetic field have only a non-vanishing $z$-component. As a result, the Kohn-Sham spinors decompose into spin-up ($\sigma =\uparrow$) and spin-down ($\sigma =\downarrow$) orbitals, i.e., $\Phi_i(\mathbf{r}) = (\varphi_{i,\uparrow}(\mathbf{r}), 0)$ or $\Phi_i(\mathbf{r}) = (0, \varphi(\mathbf{r})_{i,\downarrow})$. Within this restriction the direction of the magnetization is uniform, parallel to the $z$-direction $\mathbf{m}(\mathbf{r}) = (0, 0, m(\mathbf{r}))$. This restricted form is used in many practical applications. Then, one may reformulate SDFT in terms of only the spin densities $n_\sigma(\mathbf{r})$, because the particle density and the non-vanishing component of the magnetization can be re-expressed as

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}), \tag{4.15}$$

and

$$m(\mathbf{r}) = -\mu_B \left(n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})\right). \tag{4.16}$$

The total energy $E$ of a system of interacting electrons is then defined as a functional of the two spin densities $n_\sigma(\mathbf{r})$

$$E[n_\uparrow, n_\downarrow] = T_s[n_\uparrow, n_\downarrow] + U[n] + E_{xc}[n_\uparrow, n_\downarrow] + \sum_{\sigma=\uparrow,\downarrow} \int \mathrm{d}^3 r \; v_\sigma(\mathbf{r}) n_\sigma(\mathbf{r}) \tag{4.17}$$

where

$$T_s[n_\uparrow, n_\downarrow] = -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{j}^{N_\sigma}\int \mathrm{d}^3r\ \varphi^*_{j\sigma}(\mathbf{r})\nabla^2\varphi_{j\sigma}(\mathbf{r}) \tag{4.18}$$

is the non-interacting kinetic energy and $N_\sigma$ is the number of electrons with spin $\sigma$. $v_\sigma(\mathbf{r}) = v(\mathbf{r}) \pm \mu_B B$ (+ for $\sigma =\uparrow$, − for $\sigma =\downarrow$) is an external *spin-dependent* electrostatic potential. The single-particle orbitals $\varphi_{j\sigma}(\mathbf{r})$ in Eq. (4.18) are solutions of the Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + v_{s\sigma}(\mathbf{r})\right)\varphi_{j\sigma}(\mathbf{r}) = \varepsilon_{j\sigma}\varphi_{j\sigma}(\mathbf{r}) \tag{4.19}$$

where $j$ is a collective index for all quantum numbers except spin. The effective single particle potential for spin $\sigma$ is given by

$$v_{s\sigma}(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc\sigma}(\mathbf{r})\ , \tag{4.20}$$

where we have defined the spin-dependent exchange-correlation potential as

$$v_{xc,\sigma}(\mathbf{r}) = \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} = v_{xc}(\mathbf{r}) \pm \mu_B B_{xc}(\mathbf{r})\ . \tag{4.21}$$

Here, $v_{xc}$ is the exchange-correlation potential, and $B_{xc}(\mathbf{r})$ is the $z$-component of $\mathbf{B}_{xc}(\mathbf{r})$ (which is, by assumption, the only one different from zero). The self-consistency cycle is closed by computing the spin densities via

$$n_\sigma(\mathbf{r}) = \sum_{j=1}^{N_\sigma}|\varphi_{j\sigma}(\mathbf{r})|^2 \tag{4.22}$$

where the sum runs over the orbitals occupied in the KS ground state determinant.

Since the KS potential can now differ for the two spin-channels, the KS equation in SDFT generates a spin-unrestricted scheme, in the sense that the spin-up and spin-down orbitals may be different. Let us note that the unrestricted KS scheme of SDFT immediately leads to the restricted scheme of DFT if one considers functionals which only depend on the total electronic density of Eq. (4.15). In particular, the exchange-correlation potential is

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \tag{4.23}$$

and both the $v_{xc}$ and the total effective potential $v_s$ then are independent of the spin index $\sigma$. However, despite the spin-independence of $v_s$ and $v_{xc}$, the Kohn-Sham orbitals, being proper fermionic single-particle orbitals, still carry a spin-dependence. Clearly, the spin-unrestricted scheme reduces to the spin-restricted one for ground state with vanishing spin polarization, as found in closed-shell systems.

As we have seen in chapter 3, for orbital functionals the optimized effective potential method leads to an integral equation for the exchange-correlation potential. For simplicity, we again consider approximations of $E_{xc}$ that are functionals of the occupied orbitals only. The OEP integral equation in SDFT can then be written as

$$\sum_{j=1}^{N_\sigma} \left(\psi^*_{j\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) + c.c.\right) = 0 \; . \tag{4.24}$$

As opposed to Eq. (3.19) of ordinary DFT, one now has one OEP equation for each spin-channel, where the orbital shifts are defined as

$$\psi^*_{j\sigma}(\mathbf{r}) = \int \mathrm{d}^3r' \varphi^*_{j\sigma}(\mathbf{r}') \left(v_{xc,\sigma}(\mathbf{r}') - u_{xc,j\sigma}(\mathbf{r}')\right) G_{s,j\sigma}(\mathbf{r}', \mathbf{r}). \tag{4.25}$$

The Green's function $G_{s,j\sigma}$ of the Kohn-Sham system is defined as in Eq. (3.14), and $u_{xc,j\sigma}$ as in Eq. (3.17).

Written in the transformed form of Sec. 3.4, the two nontrivial OEP equations of collinear SDFT can also be written as [38]

$$\begin{aligned} v_{xc,\sigma}(\mathbf{r}) &= \frac{1}{2n_\sigma(\mathbf{r})} \sum_{j=1}^{N_\sigma} \Big[ |\varphi_{j\sigma}(\mathbf{r})|^2 \left(u_{xc,j\sigma}(\mathbf{r}) + (\bar{v}_{xc,j\sigma} - \bar{u}_{xc,j\sigma})\right) - \nabla \cdot (\psi^*_{j\sigma}(\mathbf{r}) \nabla \varphi_{j\sigma}(\mathbf{r})) \Big] \\ &+ c.c. \end{aligned} \tag{4.26}$$

where

$$\bar{v}_{xc,j\sigma} = \int \mathrm{d}^3r \; \varphi^*_{j\sigma}(\mathbf{r}) v_{xc,\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \tag{4.27}$$

and

$$\bar{u}_{xc,j\sigma} = \int \mathrm{d}^3r \; \varphi^*_{j\sigma}(\mathbf{r}) u_{xc,j\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \; . \tag{4.28}$$

We observe that the exchange-correlation potential of ordinary DFT given in Eq. (3.37) can then be written as a weighted average of potentials for the different spin channels

$$v_{xc}(\mathbf{r}) = \frac{n_\uparrow(\mathbf{r})\tilde{v}_{xc,\uparrow}(\mathbf{r}) + n_\downarrow(\mathbf{r})\tilde{v}_{xc,\downarrow}(\mathbf{r})}{n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})} \; , \tag{4.29}$$

where

$$\begin{aligned} \tilde{v}_{xc,\sigma}(\mathbf{r}) &= \frac{1}{2n_\sigma(\mathbf{r})} \sum_{j=1}^{N_\sigma} \Big[ |\varphi_{j\sigma}(\mathbf{r})|^2 \left(u_{xc,j\sigma}(\mathbf{r}) + (\tilde{v}_{xc,j\sigma} - \bar{u}_{xc,j\sigma})\right) - \nabla \cdot (\tilde{\psi}^*_{j\sigma}(\mathbf{r}) \nabla \varphi_{j\sigma}(\mathbf{r})) \Big] \\ &+ c.c. \end{aligned} \tag{4.30}$$

and $\tilde{v}_{xcj\sigma}$ is defined as $\bar{v}_{xcj\sigma}$ in Eq. (4.27) except that $v_{xc\sigma}$ is replaced by $v_{xc}$.

## 4.2 Current-density-functional theory

The Hamiltonian of current-density-functional theory (CDFT) includes the coupling of the electronic orbital degrees of freedom to an external vector potential $\mathbf{A}(\mathbf{r})$

$$\begin{aligned} \hat{H} &= \hat{T} + \hat{V}_{ee} + \int \mathrm{d}^3 r \; \hat{n}(\mathbf{r}) v(\mathbf{r}) + \frac{1}{c} \int \mathrm{d}^3 r \; \hat{\mathbf{j}}_p(\mathbf{r}) \mathbf{A}(\mathbf{r}) \\ &+ \frac{1}{2c^2} \int \mathrm{d}^3 r \; \hat{n}(\mathbf{r}) \mathbf{A}^2(\mathbf{r}) \; . \end{aligned} \tag{4.31}$$

Here $c$ is the speed of light. The operator of the particle density, $\hat{n}(\mathbf{r})$, is defined as in Eq. (4.2), and

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2i} \left\{ \hat{\Psi}^\dagger(\mathbf{r}) \nabla \hat{\Psi}(\mathbf{r}) - \left[ \nabla \hat{\Psi}^\dagger(\mathbf{r}) \right] \hat{\Psi}(\mathbf{r}) \right\} \tag{4.32}$$

is the the paramagnetic current density operator.

Following Vignale and Rasolt [50], a reformulation of the energy variational principle is obtained in the form

$$E_{v,\mathbf{A}} = \min_{n, \mathbf{j}_p} E_{v,\mathbf{A}}[n, \mathbf{j}_p] \tag{4.33}$$

with

$$E_{v,\mathbf{A}}[n, \mathbf{j}_p] = F[n, \mathbf{j}_p] + \int \mathrm{d}^3 r \; v(\mathbf{r}) n(\mathbf{r}) + \frac{1}{c} \int \mathrm{d}^3 r \; \mathbf{j}_p(\mathbf{r}) \mathbf{A}(\mathbf{r}) + \frac{1}{2c^2} \int \mathrm{d}^3 r \; n(\mathbf{r}) \mathbf{A}^2(\mathbf{r}) \; . \tag{4.34}$$

It appears natural to use the paramagnetic current density $\mathbf{j}_p$ as basic variable, in addition to the particle density. In particular, the universal functional $F[n, \mathbf{j}_p]$ depends on both $n$ and $\mathbf{j}_p$.

In the next step, the Kohn-Sham scheme is introduced by assuming that there exists a system of non-interacting electrons, subject to the effective potentials $(v_s, \mathbf{A}_s)$, whose ground state has same particle and paramagnetic-current density as the ground state of the given interacting system. The form of the Kohn-Sham equation is [50]

$$\left[ \frac{1}{2} \left( -i\nabla + \frac{1}{c} \mathbf{A}_s(\mathbf{r}) \right)^2 + v_s(\mathbf{r}) \right] \Phi_k(\mathbf{r}) = \epsilon_k \Phi_k(\mathbf{r}) \; . \tag{4.35}$$

As in DFT and SDFT, the functional $F[n, \mathbf{j}_p]$ can be decomposed in terms of the kinetic energy functional of non-interacting electrons, $T_s[n, \mathbf{j}_p]$, the classical electrostatic energy, $U[n]$, and the exchange-correlation energy functional, $E_{xc}[n, \mathbf{j}_p]$

$$F[n, \mathbf{j}_p] = T_s[n, \mathbf{j}_p] + U[n] + E_{xc}[n, \mathbf{j}_p] \; . \tag{4.36}$$

Then the effective potentials in the Kohn-Sham equation are given by

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + \frac{1}{2c^2} \left[ \mathbf{A}^2(\mathbf{r}) - \mathbf{A}_s^2(\mathbf{r}) \right] \; , \tag{4.37}$$

and

$$\mathbf{A}_s(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \mathbf{A}_{xc}(\mathbf{r}) \; . \tag{4.38}$$

The exchange-correlation scalar and vector potentials are defined as partial functional derivatives of $E_{xc}[n, \mathbf{j}_p]$:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n, \mathbf{j}_p]}{\delta n(\mathbf{r})}\Big|_{\mathbf{j}_p} \tag{4.39}$$

and

$$\mathbf{A}_{xc}(\mathbf{r}) = c \, \frac{\delta E_{xc}[n, \mathbf{j}_p]}{\delta \mathbf{j}_p(\mathbf{r})}\Big|_{n} \; , \tag{4.40}$$

respectively. $v_H(\mathbf{r})$ is the Hartree potential (Eq. (2.40)). The $N$ Kohn-Sham single-particle states with lowest energies are used to compute the particle density and the paramagentic current density

$$\mathbf{j}_p(\mathbf{r}) = \frac{1}{2i} \sum_{k=1}^{N} \left\{ \Phi_k^\dagger(\mathbf{r}) \nabla \Phi_k(\mathbf{r}) - \left[ \nabla \Phi_k^\dagger(\mathbf{r}) \right] \Phi_k(\mathbf{r}) \right\} \; . \tag{4.41}$$

All the elements needed to evaluate the ground state energy $E_{v,\mathbf{A}}$ for the interacting electrons are available.

### 4.2.1 Kohn-Sham scheme and gauge transformations

In this section we consider the transformation

$$v(\mathbf{r}) \longrightarrow v(\mathbf{r}), \quad \mathbf{A}(\mathbf{r}) \longrightarrow \mathbf{A}(\mathbf{r}) + \nabla \Lambda(\mathbf{r}) \; . \tag{4.42}$$

If the many-body wavefunction is transformed accordingly as

$$\Psi \longrightarrow \exp[-\frac{i}{c} \sum_{k=1}^{N} \Lambda(\mathbf{r}_k)] \Psi \tag{4.43}$$

the form of the Schrödinger equation is preserved. Then note that the particle density and paramagnetic-current density transform as

$$n(\mathbf{r}) \longrightarrow n(\mathbf{r}) \; , \quad \mathbf{j}_p(\mathbf{r}) \longrightarrow \mathbf{j}_p(\mathbf{r}) - \frac{1}{c} n(\mathbf{r}) \nabla \Lambda(\mathbf{r}), \tag{4.44}$$

i.e., the paramagnetic-current density is not a gauge invariant quantity. This leads to the necessity of verify whether the Kohn-Sham scheme of CDFT is invariant under the gauge transformation defined just above.

Eqs. (4.34) and (4.44) imply that $F[n, \mathbf{j}_p(\mathbf{r})]$ transforms as

$$F[n, \mathbf{j}_p - \frac{1}{c} n \nabla \Lambda] = F[n, \mathbf{j}_p(\mathbf{r})] - \frac{1}{c} \int d\mathbf{r} \mathbf{j}_p(\mathbf{r}) \cdot \nabla \Lambda(\mathbf{r}) + \frac{1}{2c^2} \int d\mathbf{r} n(\mathbf{r}) |\nabla \Lambda(\mathbf{r})|^2. \tag{4.45}$$

This is apparent if we consider the definition of $F[n, \mathbf{j}_p]$. In Levy's constrained-search formulation this functional can be defined as

$$F[n, \mathbf{j}_p] := \inf_{\Psi \to n, \mathbf{j}_p} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \quad \text{with } \Psi \in \mathbf{W_N} \text{ and } n, \mathbf{j}_p \in \mathbf{D'_N}. \tag{4.46}$$

In this definition $\mathbf{D'_N}$ is the set that contains all particle and paramagnetic current densities which are N-representable. It is not necessary to ask for the paramagnetic-current density to satisfy the continuity equation. In fact, as we will see below, this condition will be automatically satisfied.

It is readily seen that $T_s[n, \mathbf{j}_p(\mathbf{r})]$ transforms as $F[n, \mathbf{j}_p(\mathbf{r})]$, since it differs from the latter by a gauge invariant term (the electron-electron interaction). Alternatively, this can also be seen by transforming the non-interacting wavefunction as dictated by transformation (4.43). The Hartree energy, $U$, only depending on $n$ is invariant. As a consequence it is immediately seen that also $E_{xc}$ is invariant, i.e.,

$$E_{xc}[n, \mathbf{j}_p - \frac{1}{c} n \nabla \Lambda] = E_{xc}[n, \mathbf{j}_p(\mathbf{r})]. \tag{4.47}$$

A simple gauge-invariant quantity depending on both $\mathbf{j}_p$ and $n$ is the vorticity density

$$\mathbf{v}(\mathbf{r}) = \nabla \times \frac{\mathbf{j}_p(\mathbf{r})}{n(\mathbf{r})} \, . \tag{4.48}$$

Thus the exchange-correlation energy functional can depend on $\mathbf{j}_p$ only through the vorticity

$$E_{xc}[n, \mathbf{j}_p] = \tilde{E}_{xc}[n, \mathbf{v}]. \tag{4.49}$$

In terms of $n$ and $\mathbf{v}$, we then have

$$v_{xc}(\mathbf{r}) = \frac{\delta \tilde{E}_{xc}}{\delta n(\mathbf{r})} = \tilde{v}_{xc}(\mathbf{r}) - \frac{1}{c} \mathbf{A}_{xc}(\mathbf{r}) \cdot \frac{\mathbf{j}_p(\mathbf{r})}{n(\mathbf{r})}, \tag{4.50}$$

where

$$\tilde{v}_{xc}(\mathbf{r}) = \frac{\delta \tilde{E}_{xc}}{\delta n(\mathbf{r})}\Big|_{\mathbf{v}} \tag{4.51}$$

and

$$\mathbf{A}_{xc}(\mathbf{r}) = -c \frac{1}{n(\mathbf{r})} \nabla \times \frac{\delta \tilde{E}_{xc}}{\delta \mathbf{v}(\mathbf{r})}\Big|_{\mathbf{n}}. \tag{4.52}$$

Both $\tilde{v}_{xc}$ and $\mathbf{A}_{xc}(\mathbf{r})$ are gauge-invariant, since their definitions involve only gauge-invariant quantities. Also note that

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + \tilde{v}_{xc}(\mathbf{r}) + \frac{1}{c} \mathbf{A}_{xc}(\mathbf{r}) \cdot \frac{\mathbf{j}(\mathbf{r})}{n(\mathbf{r})} - \frac{1}{2c^2} \mathbf{A}^2_{xc}(\mathbf{r}), \tag{4.53}$$

where

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r}) + \frac{1}{c} n(\mathbf{r}) \mathbf{A}(\mathbf{r}) \tag{4.54}$$

is the total physical current, which is gauge invariant. It is then clear that the gauge transformations defined above induce a similar transformation for the effective fields $v_s$ and $\mathbf{A}_s$, and the form of the Kohn-Sham equation is indeed preserved.

Finally note that the total Kohn-Sham current density

$$\mathbf{j}_s(\mathbf{r}) := \mathbf{j}_p(\mathbf{r}) + \frac{1}{c} n(\mathbf{r}) \mathbf{A}_s(\mathbf{r}) = \mathbf{j}(\mathbf{r}) + \frac{1}{c} n(\mathbf{r}) \mathbf{A}_{xc}(\mathbf{r}) \tag{4.55}$$

may not be equal to the physical current $\mathbf{j}$. In fact, an additional term from the exchange-correlation part of the effective vector potential appears in Eq. (4.55).

The Schrödinger form of the Kohn-Sham equation guarantees that the Kohn-Sham total current is source free. That is, it satisfies the (static) continuity equation. Alternatively, because of Eq. (4.52) it is clear that

$$\nabla \cdot (n(\mathbf{r}) \mathbf{A}_{xc}(\mathbf{r})) = 0, \tag{4.56}$$

which again leads to

$$\nabla \cdot \mathbf{j}_s = \nabla \cdot \mathbf{j} = 0. \tag{4.57}$$

### 4.2.2 Local vorticity approximations for $E_{xc}$

The local density approximation (LDA) [4] and the local-spin-density approximation (LSDA) [4, 49] use as paradigm system the homogeneous electron-gas. The idea is that a inhomogeneous system may be locally represented as a uniform or slowly varying one. Although this approach appears rather crude for real systems (which are typically far from the slowly-varying limit), it works surprisingly well. While the LDA and LSDA are well known to the practitioners of DFT and SDFT, the corresponding approximation for CDFT is less popular. Hence, we here outline its main ingredients. For reasons that will become clear below, it is also known as the local vorticity approximation (LVA).

Let us consider an electron-gas exposed to an external magnetic field. For weak external magnetic field, the ground state energy per electron of the uniform electron gas may be written up to second order in the $\mathbf{B}$-field as

$$\epsilon(n, \mathbf{B}) = \epsilon(n, 0) - \frac{1}{2n} \chi_L(n) |\mathbf{B}|^2 + \dots \,, \tag{4.58}$$

where $\chi_L(n)$ is the diamagnetic susceptibility of the interacting system. This expression can be rewritten in terms of the vorticity density as

$$\epsilon(n, \mathbf{v}) = \epsilon(n, 0) - \frac{1}{2nc^2} \chi_L(n) |\mathbf{v}|^2 \,, \tag{4.59}$$

with $\mathbf{v}$ being the vorticity (see Eq. (4.48)), by observing that for the uniform gas $\mathbf{j}$ vanishes identically, and thus the external field can be expressed as

$$\mathbf{A} = -c \, \frac{\mathbf{j}_p}{n} \implies \mathbf{B} = \nabla \times \mathbf{A} = -c \, \mathbf{v} \,, \tag{4.60}$$

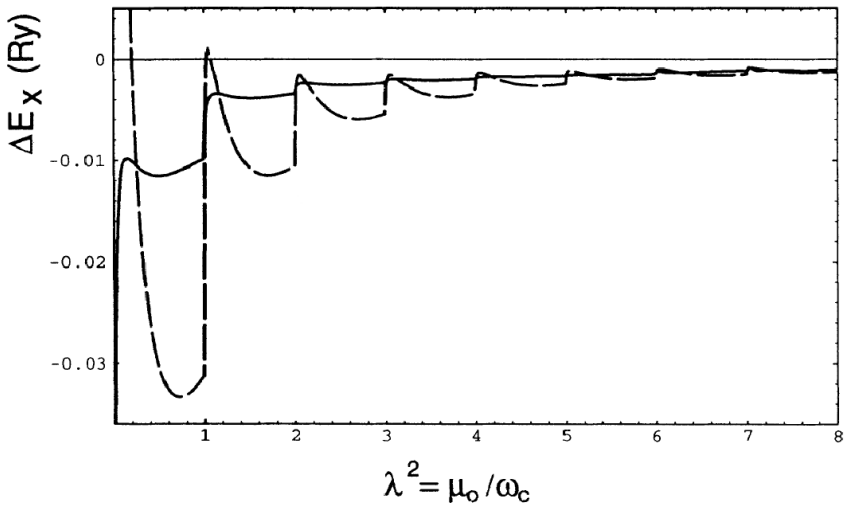


Figure 4.1: *Difference between the exchange energy with and without magnetic field (dashed line) calculated at constant density (corresponding to $r_s = 1$). The solid line represents this difference for the full exchange-correlation energy. The horizontal axis represents the chemical potential in units of the cyclotron frequency ($\omega_c = \frac{eB}{mc}$). Plot extracted from Ref. [51].*

In the last step, making use of perturbation theory for the non-interacting kinetic energy as well, the second-order shift for the xc-energy per particle can be expressed as [52]

$$\epsilon_{xc}(n, \mathbf{j}_p) = \epsilon_x(n) \left[ \frac{1}{18\pi n} \left( 1 - \frac{\chi_L(n)}{\chi_L^0(n)} \right) |\mathbf{v}|^2 \right] , \tag{4.61}$$

where $\epsilon_x(n)$ is the exchange energy per electron of the uniform gas, and $\chi_L^0(n) = -v_F/(12\pi^2 c^2)$ ($v_F$ is the Fermi velocity).

Note that, since for the uniform gas $\mathbf{j} = 0$, using $\mathbf{j}$, rather than $\mathbf{j}_p$, as basic variable would not have allowed us to obtain an LDA-type approximation of any kind. However Eq. (4.61) is valid only for small vorticity fields. Going beyond this limitation, the random phase approximation (RPA) applied to the electron gas with magnetic field has been used [51] to construct an LVA. Figs. 4.1 and 4.2 show that, in contrast to the small vorticity limit of Eq. (4.61), the exchange and correlation energies exhibit a characteristic series of cusps corresponding of successive Landau

subbands. At increasing magnetic field strength, which correspond to increasing value of the vorticity density, the difference with respect to the exchange-correlation energy at zero field becomes more and more important.

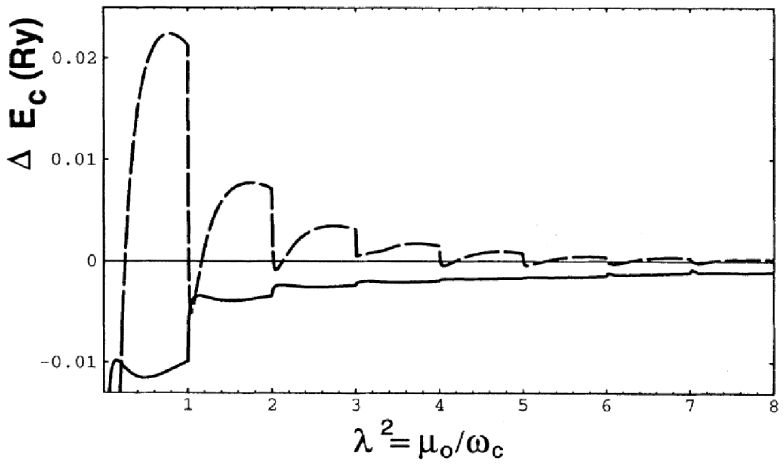


Figure 4.2: *Difference between the correlation energy with and without magnetic field (dashed line) calculated at constant density (corresponding to $r_s = 1$). The solid lines represent this difference for the full exchange-correlation energy. The horizontal axis represents the chemical potential in units of the cyclotron frequency ($\omega_c = \frac{eB}{mc}$). Plot extracted from [51].*

We now address the application of the above LVA functionals to inhomogeneous systems. Of particular interest is the situation where, at vanishing external magnetic field, the system is in a state with paramagnetic current different from zero. This can occur for a system having degenerate ground states such as open-shell atoms. Applying the LVA would correspond in this case to consider the inhomogeneous electron gas as a locally homogeneous one, which is exposed to an effective magnetic field generating the given local vorticity. This suggests that even at zero external magnetic field, a careful consideration of the orbital currents for the exchange-correlation functionals may be important. We will extensively consider this point in Chap. 6, in connection with a well-known problem of DFT which is generally known as the "degeneracy problem". But before this, let us also note that the cusps in Figs. 4.1

and 4.2 immediately point at possible numerical problems when computing the effective potentials within the corresponding local approximation [53]. These problems can be avoided by introducing some regularizations, which smooth out the cusps [53, 54, 55], although this introduces additional approximations. Alternatively, the fact that the cusps occur at the occupation of different Landau levels suggest that such numerical problems may be automatically handled by considering expressions for $E_{xc}$ which depend explicitly on the Kohn-Sham orbitals rather than on the particle and vorticity densities [53, 56, 57]. This is indeed one of the ideas that will bring us to chapter 5.

## 4.3 Current-spin-density-functional theory

Having discussed SDFT and CDFT, we can briefly report the basic equations of current-spin-density-functional theory (CSDFT). Here, the complete (non-relativistic) Hamiltonian is considered. In second quantization and atomic units, it reads

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V}_{ee} + \int \mathrm{d}^3 r\ \hat{n}(\mathbf{r}) v(\mathbf{r}) - \int \mathrm{d}^3 r\ \hat{\mathbf{m}}(\mathbf{r}) \mathbf{B}(\mathbf{r}) \\ &\quad + \frac{1}{c} \int \mathrm{d}^3 r\ \hat{\mathbf{j}}_p(\mathbf{r}) \mathbf{A}(\mathbf{r}) + \frac{1}{2c^2} \int \mathrm{d}^3 r\ \hat{n}(\mathbf{r}) \mathbf{A}^2(\mathbf{r}) \ . \end{aligned} \tag{4.62}$$

The corresponding energy functional [52] is

$$\begin{aligned} E_{v,\mathbf{B},\mathbf{A}}[n, \mathbf{m}, \mathbf{j}_p] &= F[n, \mathbf{m}, \mathbf{j}_p] + \int \mathrm{d}^3 r\ v(\mathbf{r}) n(\mathbf{r}) - \int \mathrm{d}^3 r\ \mathbf{m}(\mathbf{r}) \mathbf{B}(\mathbf{r}) \\ &\quad + \frac{1}{c} \int \mathrm{d}^3 r\ \mathbf{j}_p(\mathbf{r}) \mathbf{A}(\mathbf{r}) + \frac{1}{2c^2} \int \mathrm{d}^3 r\ n(\mathbf{r}) \mathbf{A}^2(\mathbf{r}) \ . \end{aligned} \tag{4.63}$$

Assuming that the Kohn-Sham ground state is a single Slater determinant, the corresponding spinor-orbitals are given by the following eigenvalue problem

$$\left[ \frac{1}{2} \left( -i\nabla + \frac{1}{c} \mathbf{A}_s(\mathbf{r}) \right)^2 + v_s(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \mathbf{B}_s(\mathbf{r}) \right] \Phi_k(\mathbf{r}) = \epsilon_k \Phi(\mathbf{r}) \ . \tag{4.64}$$

The effective fields can be expressed as

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + \frac{1}{2c^2} \left[ \mathbf{A}^2(\mathbf{r}) - \mathbf{A}_s^2(\mathbf{r}) \right] \ , \tag{4.65}$$

$$\mathbf{B}_s(\mathbf{r}) = \mathbf{B}(\mathbf{r}) + \mathbf{B}_{xc}(\mathbf{r}) \ , \tag{4.66}$$

$$\mathbf{A}_s(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \mathbf{A}_{xc}(\mathbf{r}) \ , \tag{4.67}$$

and, as usual, $v_H$ is the Hartree potential (see Eq. (2.40)). The exchange-correlation potentials are functional derivatives of the exchange-correlation energy $E_{xc}$ with respect to the corresponding conjugate densities

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n, \mathbf{m}, \mathbf{j}_p]}{\delta n(\mathbf{r})} \Big|_{\mathbf{m},\ \mathbf{j}_p} \ , \tag{4.68}$$

$$\mathbf{B}_{xc}(\mathbf{r}) = -\frac{\delta E_{xc}[n, \mathbf{m}, \mathbf{j}_p]}{\delta \mathbf{m}(\mathbf{r})}\Big|_{n,\ \mathbf{j}_p}, \tag{4.69}$$

$$\mathbf{A}_{xc}(\mathbf{r}) = c\ \frac{\delta E_{xc}[n, \mathbf{m}, \mathbf{j}_p]}{\delta \mathbf{j}_p(\mathbf{r})}\Big|_{n,\ \mathbf{m}}. \tag{4.70}$$

Before concluding, an observation is in order. The external *physical* magnetic field $\mathbf{B}$ is connected to the external vector potential $\mathbf{A}$ through the relation

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{4.71}$$

In this respect, it is important to note that Eq. (4.71) does not automatically apply to the *effective* fields. First of all, in CSDFT as formulated by Vignale and Rasolt [52], the set of the external *physical* magnetic fields, and thus the set of corresponding physical ground state densities, are a sub-set of all the possible external fields and ground state densities that can be *formally* considered. Second, the relation (4.71) does not enter explicitly in the definition of the functionals. Third, the Kohn-Sham scheme is introduced by requiring that (n,$\mathbf{m}$,$\mathbf{j}_p$) are non-interacting ($v$,$\mathbf{B}$,$\mathbf{A}$)-representable - rather than specifying the more restrictive condition to be ($v$,$\mathbf{B} = \nabla \times \mathbf{A}$,$\mathbf{A}$)-representable. In passing, we also observe that in the non-relativistic framework it is quite natural to think of the spin- and orbital-degree of freedoms as independent (decoupled) quantities. This is reflected in the scheme of CSDFT by considering the magnetization density and the paramagnetic-current density as independent quantities to which correspond independent fields in the sense just specified above. All these aspects will be further analyzed in the next section, and then again in Sec. 5.2.

## 4.4 From DFT to CSDFT

Conceptually, DFT, SDFT, and CSDFT are very similar: they all map the system of interacting electrons onto a system of non-interacting particles moving in some effective fields. In the case of DFT this auxiliary system yields the same electron density as the interacting one, while in SDFT the magnetization densities of the two systems coincide as well. In CSDFT, also the paramagnetic current density of the auxiliary system is equal to the paramagnetic current density of the interacting system. In all three formalisms the energy of the interacting system is written as a functional of the corresponding densities and the value for the ground state energy is obtained by minimizing this functional with respect to the densities. But going from DFT to CSDFT, the domain of the functionals changes: it is enlarged, and the effective fields increase in number. Thus - although the adopted notation does not stress this point - the $v_{xc}$ of DFT is not the same as the $v_{xc}$ in the other frameworks, as the $\mathbf{B}_{xc}$ in SDFT cannot be expected to be the same as the $\mathbf{B}_{xc}$ in CSDFT. But intuitively some equivalences (for particular states or systems) can be expected. In this sense, there is an important case to be carefully considered. This

is the case of zero external $\mathbf{B}$ and $\mathbf{A}$ fields. In this limit, only $\mathbf{B}_{xc}$ and $\mathbf{A}_{xc}$ can still contribute. Non-vanishing $\mathbf{A}_{xc}$ can be expected for ground states having non-vanishing paramagnetic current, while a non-vanishing $\mathbf{B}_{xc}$ will result for ground states with magnetization different from zero.

It is also interesting to note that in the limit of vanishing external magnetic field, DFT, SDFT and CSDFT can all be applied and, with the exact functionals, would yield the same total energy. But as the experience with the LDA and LSDA (respectively in DFT and SDFT) tells, within a given type of approximations, different numerical results are obtained [58]. In particular, for states having a finite magnetization, it is usually better to employ the LSDA rather than LDA. This reflects the fact that LSDA is built to deal with spin-polarized ground states, while the LDA is developed for states with vanishing magnetization. We may then expect additional benefits in developing approximations for functionals which take into account that ground states can have a non-vanishing current as well. It is indeed one of the aims of this work, to further investigate this issue, in particular when orbital functionals are used.

### 4.4.1 Non-uniqueness problem

In going from DFT to CSDFT one faces what at first may seem a shocking surprise: The Hohenberg-Kohn theorem as stated in DFT is not valid anymore. In particular, the one-to-one correspondence between the sets of external potentials and ground state densities is missing. Of course, also in DFT there is an infinite number of potentials that yield the same ground state density, but they differ only by a trivial additive constant. Instead, in SDFT, CDFT and CSDFT they can differ in a non-trivial way. This difference was already pointed out in the work by von Barth and Hedin [49] where SDFT was introduced. This was later confirmed, and extensively investigated by Eschrig and Pickett [59]. The same problem was further analyzed by Ullrich [60] for SDFT on arbitrary lattices, leading to other non-trivial examples of nonuniqueness. Finally, additional constructions of set of potentials which give the same ground state densities have been reported for both SDFT and CDFT by Capelle and Vignale [61, 62]. Form the latter works, we take a couple of clarifying examples.

To obtain a condition for nonuniqueness in SDFT, let us consider $v' = v + \Delta v$ and $\mathbf{B}' = \mathbf{B} + \Delta\mathbf{B}$ that are supposed to give the same (many-body) ground state $|\Psi\rangle$ as $v$ and $\mathbf{B}$. In particular, we have in mind a system with an energy gap between the ground and the first excited state, and with total magnetization $\hat{M}_z = \int d^3r\ \hat{m}_z(\mathbf{r})$ as a constant of motion ($\hat{M}_z$ commutes with the Hamiltonian). Thus, the choice $v' = v$ and $\Delta\mathbf{B} = C\mathbf{u}_z$ (where $\mathbf{u}_z$ is a unit vector in the $z$ direction) is a proper one as long as $C$ is not large enough to induce level crossings.

As an additional example, we consider the case of a fully polarized ground state. In this situation, all the electrons are in the same spin state, say spin up: $N = N_\uparrow$, and thus $N_\downarrow = 0$. While the part of the effective potential for the $N_\uparrow$ orbitals is

determined (for finite systems the corresponding additive constant can be chosen in such a way that the potential goes to zero at infinity), the potential for $N_\downarrow$ orbitals is completely undetermined, as long as its lowest eigenvalue is higher than the $N_\uparrow$th eigenvalues of the corresponding spin-up equation.

Similarly for CDFT [61, 62], let us consider $v' = v + \Delta v$ and $\mathbf{A}' = \mathbf{A} + \Delta\mathbf{A}$ such that the same ground state, $|\Psi\rangle$, as for $v$ and $\mathbf{A}$ is obtained. Then necessary condition is

$$\int d^3r \left[\hat{n}\Delta v + \frac{1}{2c^2}\Delta\mathbf{A}^2 + \frac{1}{c}\hat{\mathbf{j}}_p\Delta\mathbf{A}\right]|\Psi\rangle = \Delta E|\Psi\rangle \ . \tag{4.72}$$

As a trivial example we may consider the class of systems for which $\hat{N} = \int d^3r\ \hat{n}$ is a constant of motion. Then $\Delta v$ is constant, and $\Delta\mathbf{A} = 0$ is a solution of condition (4.4.1). This is the well-known, and harmless, nonuniqueness of the scalar potential with respect to the additional constant.

A less trivial example is obtained by considering a system with an energy gap between the ground state and the first excited one, and for which

$$\hat{L}_z = \int d^3r\,(\mathbf{u}_z \times \hat{\mathbf{r}}) \cdot \hat{\mathbf{j}}_p \tag{4.73}$$

is a constant of motion. Thus, solutions of condition (4.4.1) are given in the form of $\Delta\mathbf{A} = C(\mathbf{u}_z \times \mathbf{r})$ and $\Delta v = -\frac{(\Delta\mathbf{A})^2}{2c}$, with $C$ being a constant not large enough to induce level crossings.

A reassurance that the problem is not a real impediment for SDFT has been given by Kohn, Savin and Ullrich [63]. More recently, Gidopoulos reported an analysis showing that the problem does not exist in SDFT for the class of non-collinear magnetic fields [64].

At last, the problem has recently been analyzed in combination with the degeneracy of ground states in Ref. [65]. It is seen that, Hohenberg-Kohn functionals for SDFT, CDFT and CSDFT can still be defined without impediment. Although in the Hohenberg-Kohn formulation it is not trivially seen that the functionals can be still defined, in passing we observe that in the Levy formulation it is instead apparent. In fact, in the latter formulation neither the one-to-one correspondence between wavefunctions and densities nor the one-to-one correspondence among densities external potentials is used in defining the functionals. However, as well as in the Hohenberg-Kohn formulation, the problem may have some important, and negative, impacts when the differentiability of the functionals is considered, or invoked. This is still an open problem. It is connected with the non-interacting v-representability question of the interacting densities. Furthermore, it may enter in the extension of the OEP method to SDFT and C(S)DFT. Thus we will reconsider it in the next chapters.

## 4.5 Different formulation of CSDFT: $\mathbf{j}_m$-DFT

One can formulate CSDFT in different ways. For example, it is possible to introduce a spin-dependent vector potential $\mathbf{A}_\sigma$ [52]. Correspondingly, spin-dependent

paramagnetic-current densities have to be taken as basic densities. Another example is the formulation of Diener [66], which contemplates as basic density the total current in place of the paramagnetic one. Along these lines, we look at yet another formulation - which we call the $\mathbf{j}_m$-formulation [67].

Let us start from the Hamiltonian of Eq. (4.62) and specify that we restrict the field $\mathbf{B}$ and $\mathbf{A}$ to satisfy Eq. (4.71). In order to make it explicit, we rewrite the Hamiltonian as follows

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V}_{ee} + \int \mathrm{d}^3 r\, \hat{n}(\mathbf{r}) v(\mathbf{r}) - \int \mathrm{d}^3 r\, \hat{\mathbf{m}}(\mathbf{r}) \left[\nabla \times \mathbf{A}(\mathbf{r})\right] \\ &\quad + \frac{1}{c} \int \mathrm{d}^3 r\, \hat{\mathbf{j}}_p(\mathbf{r}) \mathbf{A}(\mathbf{r}) + \frac{1}{2c^2} \int \mathrm{d}^3 r\, \hat{n}(\mathbf{r}) \mathbf{A}^2(\mathbf{r}) \,. \end{aligned} \tag{4.74}$$

Integrating by parts the Zeeman term and *assuming* that the surface contributions vanishes (which is certainly reasonable for finite system) we obtain

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \int \mathrm{d}^3 r\, \hat{n}(\mathbf{r}) \left[ v(\mathbf{r}) + \frac{1}{2c^2} \mathbf{A}(\mathbf{r}) \right] + \int \mathrm{d}^3 r\, \hat{\mathbf{j}}_m(\mathbf{r}) \mathbf{A}(\mathbf{r}) \tag{4.75}$$

where

$$\hat{\mathbf{j}}_m(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) - c \nabla \times \hat{\mathbf{m}}(\mathbf{r}). \tag{4.76}$$

Expressions (4.75) and (4.76) suggest that the ground state problem can be "density functionalized" by choosing $(n, \mathbf{j}_m)$ as basic densities. This leads to the following energy functional [67]

$$\begin{aligned} E_{v,\mathbf{A}}[n, \mathbf{j}_m] &= F[n, \mathbf{j}_m] + \int \mathrm{d}^3 r\, v(\mathbf{r}) n(\mathbf{r}) + \frac{1}{c} \int \mathrm{d}^3 r\, \mathbf{j}_m(\mathbf{r}) \mathbf{A}(\mathbf{r}) \\ &\quad + \frac{1}{2c^2} \int \mathrm{d}^3 r\, n(\mathbf{r}) \mathbf{A}^2(\mathbf{r}) \,. \end{aligned} \tag{4.77}$$

The Kohn-Sham scheme is introduced by assuming that the ground state densities $(n, \mathbf{j}_m)$ of the interacting system are non-interacting $(v, \mathbf{A}, \mathbf{B} = \nabla \times \mathbf{A})$-representable. Therefore, the Kohn-Sham equation is

$$\left[ \frac{1}{2} \left( -i\nabla + \frac{1}{c} \mathbf{A}_s(\mathbf{r}) \right)^2 + v_s(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \mathbf{B}_s(\mathbf{r}) \right] \Phi_k(\mathbf{r}) = \epsilon_k \Phi(\mathbf{r}) \,. \tag{4.78}$$

Thus by construction the effective magnetic field is a quantity derived from the effective vector potential

$$\mathbf{B}_s(\mathbf{r}) := \nabla \times \mathbf{A}_s(\mathbf{r}) \,. \tag{4.79}$$

The basic effective fields are the scalar potential

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + \frac{1}{2c^2} \left[ \mathbf{A}^2(\mathbf{r}) - \mathbf{A}_s^2(\mathbf{r}) \right] \,, \tag{4.80}$$

and the effective vector potential

$$\mathbf{A}_s(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \mathbf{A}_{xc}(\mathbf{r}). \tag{4.81}$$

In particular,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n, \mathbf{j}_m]}{\delta n(\mathbf{r})}\Big|_{\mathbf{j}_m} , \tag{4.82}$$

$$\mathbf{A}_{xc}(\mathbf{r}) = c\, \frac{\delta E_{xc}[n, \mathbf{j}_m]}{\delta \mathbf{j}_m(\mathbf{r})}\Big|_{n} . \tag{4.83}$$

It is readily seen that

$$\mathbf{B}_{xc}(\mathbf{r}) := \nabla \times \mathbf{A}_{xc}(\mathbf{r}) . \tag{4.84}$$

We here conclude our review of different "flavors" of density-functional theory. In the following chapters we will report our developments and results.

# Chapter 5

# Extensions of the OEP method

As we have discussed in chapter 3, there are several motivations for considering approximations to the exchange and correlation energies in terms of the Kohn-Sham orbitals. When dealing with magnetic properties of many-electron systems, this choice seems even more necessary. This is related to the fact that, although it is possible to construct a LDA-type approximation for CDFT [50, 51, 52], the same approximation (and consequentially the ones based on it) are awkward to use in practical calculations. This has a clear physical reason: when a uniform electron gas is exposed to an external magnetic field, Landau levels form and, for given magnetic field, the xc energy density exhibits derivative discontinuities as function of the density whenever a new Landau level is filled. In a local approximation these discontinuities then show up in the corresponding exchange-correlation potentials at those points in space where the local densities coincide with the densities of the uniform gas for which these discontinuities occur. One solution to this problem is to smoothly interpolate the exchange-correlation energy density between the limits of weak and strong magnetic fields [54, 55]. Alternatively, since the problem is entirely due to the orbital effect of occupying Landau levels, it is attractive to use explicitly orbital-dependent approximations to $E_{xc}$. Moreover, a natural non-collinear description is immediately obtained if one accepts to employ exchange-correlation functionals which explicitly depend on two-component Kohn-Sham spinors, without further restricting their form.

## 5.1 OEP method in CSDFT

The calculation of the exchange-correlation potential for orbital-dependent functionals in ordinary (S)DFT is done in the framework of the optimized effective potential method [38, 43, 44]. Here we extend this method to CSDFT and derive the OEP integral equations for the exchange-correlation potentials within a full non-collinear treatment. We start by calculating the functional derivatives of $E_{xc}$ with respect to the three effective and *independent* potentials $v_s$, $\mathbf{B}_s$, and $\mathbf{A}_s$ [68]. These functional

derivatives can be computed in two different ways by using the chain rule, i.e.,

$$\begin{aligned}\frac{\delta E_{xc}}{\delta v_s(\mathbf{r})} &= \int \mathrm{d}^3r' \left[ v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \frac{1}{c}\mathbf{A}_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta v_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta v_s(\mathbf{r})} \right] \\ &= \sum_{i=1}^{N} \int \mathrm{d}^3r' \left[ \frac{\delta E_{xc}}{\delta \Phi_i(\mathbf{r}')} \frac{\delta \Phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} + h.c. \right], \end{aligned} \tag{5.1}$$

$$\begin{aligned}\frac{\delta E_{xc}}{\delta \mathbf{B}_s(\mathbf{r})} &= \int \mathrm{d}^3r' \left[ v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + \frac{1}{c}\mathbf{A}_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} \right] \\ &= \sum_{i=1}^{N} \int \mathrm{d}^3r' \left[ \frac{\delta E_{xc}}{\delta \Phi_i(\mathbf{r}')} \frac{\delta \Phi_i(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + h.c \right], \end{aligned} \tag{5.2}$$

$$\begin{aligned}\frac{\delta E_{xc}}{\delta \mathbf{A}_s(\mathbf{r})} &= \int \mathrm{d}^3r' \left[ v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} + \frac{1}{c}\mathbf{A}_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} \right] \\ &= \sum_{i=1}^{N} \int \mathrm{d}^3r' \left[ \frac{\delta E_{xc}}{\delta \Phi_i(\mathbf{r}')} \frac{\delta \Phi_i(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} + h.c. \right]. \end{aligned} \tag{5.3}$$

Eqs. (5.1) - (5.3) constitute a system of coupled integral equations for the unknown exchange-correlation potentials. For simplicity, we have assumed that the approximation for $E_{xc}$ depends only on the occupied spinor orbitals such as, e.g., the exact-exchange functional

$$E_x^{EXX}[\{\Phi_i\}] = -\frac{1}{2} \sum_{i,j}^{\mathrm{occ}} \int \mathrm{d}^3r \int \mathrm{d}^3r' \, \frac{\Phi_i^\dagger(\mathbf{r}) \Phi_j(\mathbf{r}) \Phi_j^\dagger(\mathbf{r}') \Phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{5.4}$$

For any approximation of $E_{xc}$ given explicitly in terms of the spinor orbitals, the functional derivatives of $E_{xc}$ with respect to these spinors can be evaluated right away. The other functional derivatives in Eqs. (5.1) - (5.3) may be computed exactly from first-order perturbation theory by considering variations of the Kohn-Sham spinors due to a perturbation $\delta \hat{H}_s(\mathbf{r}')$ of the Kohn-Sham Hamiltonian. To first order in the perturbation these variations are

$$\delta \Phi_i(\mathbf{r}) = \sum_{\substack{j=1 \\ j \neq i}}^{\infty} \frac{\Phi_j(\mathbf{r})}{\epsilon_i - \epsilon_j} \int d^3r' \Phi_j^\dagger(\mathbf{r}') \delta \hat{H}_s(\mathbf{r}') \Phi_i(\mathbf{r}') \, , \tag{5.5}$$

where for simplicity we have assumed a non-degenerate spectrum. For arbitrary variations $\delta v_s(\mathbf{r})$, $\delta \mathbf{B}_s(\mathbf{r})$, and $\delta \mathbf{A}_s(\mathbf{r})$ in the three effective potentials, the perturbation $\delta H_s(\mathbf{r})$ is given by

$$\delta \hat{H}_s(\mathbf{r}) = \delta v_s(\mathbf{r}) + \frac{1}{2ic} \nabla \delta \mathbf{A}_s(\mathbf{r}) + \frac{1}{ic} \delta \mathbf{A}_s(\mathbf{r}) \nabla + \frac{1}{c^2} \mathbf{A}_s(\mathbf{r}) \delta \mathbf{A}_s(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \delta \mathbf{B}_s(\mathbf{r}) \, . \tag{5.6}$$

Insertion into Eq. (5.5) allows us to identify the functional derivatives of the spinors with respect to the effective potentials as

$$\frac{\delta\Phi_i(\mathbf{r})}{\delta v_s(\mathbf{r}')} = \sum_{\substack{j=1\\ j\neq i}}^{\infty} \frac{\Phi_j(\mathbf{r})}{\epsilon_i - \epsilon_j} \left[\Phi_j^\dagger(\mathbf{r}')\Phi_i(\mathbf{r}')\right] \ , \tag{5.7}$$

$$\frac{\delta\Phi_i(\mathbf{r})}{\delta \mathbf{B}_s(\mathbf{r}')} = \mu_B \sum_{\substack{j=1\\ j\neq i}}^{\infty} \frac{\Phi_j(\mathbf{r})}{\epsilon_i - \epsilon_j} \left[\Phi_j^\dagger(\mathbf{r}')\boldsymbol{\sigma}\Phi_i(\mathbf{r}')\right] \ , \tag{5.8}$$

and

$$\frac{\delta\Phi_i(\mathbf{r})}{\delta \mathbf{A}_s(\mathbf{r}')} = \sum_{\substack{j=1\\ j\neq i}}^{\infty} \frac{\Phi_j(\mathbf{r})}{\epsilon_i - \epsilon_j} \left\{ \frac{1}{2ic}\left[\Phi_j^\dagger(\mathbf{r}')\nabla'\Phi_i(\mathbf{r}') - \left(\nabla'\Phi_j^\dagger(\mathbf{r}')\right)\Phi_i(\mathbf{r}')\right] + \frac{1}{c^2}\mathbf{A}_s(\mathbf{r}')\Phi_j^\dagger(\mathbf{r}')\Phi_i(\mathbf{r}')\right\}. \tag{5.9}$$

From Eqs. (5.7) - (5.9) one can compute the static response functions, i.e., the functional derivatives of the densities with respect to the effective potentials. Inserting everything into Eqs. (5.1) - (5.3) one can then write the OEP integral equations in a very compact form as

$$\sum_{i=1}^{N} \Phi_i^\dagger(\mathbf{r})\Psi_i(\mathbf{r}) + h.c. = 0 \ , \tag{5.10}$$

$$-\mu_B \sum_{i=1}^{N} \Phi_i^\dagger(\mathbf{r})\boldsymbol{\sigma}\Psi_i(\mathbf{r}) + h.c. = 0 \ , \tag{5.11}$$

and

$$\frac{1}{2i}\sum_{i=1}^{N} \left\{\Phi_i^\dagger(\mathbf{r})\nabla\Psi_i(\mathbf{r}) - \left[\nabla\Phi_i^\dagger(\mathbf{r})\right]\Psi_i(\mathbf{r})\right\} + h.c. = 0 \ , \tag{5.12}$$

where we have defined the so-called orbital shifts [38, 39]

$$\Psi_i(\mathbf{r}) = \sum_{\substack{j=1\\ j\neq i}}^{\infty} \frac{\Phi_j(\mathbf{r})D_{ij}}{\epsilon_i - \epsilon_j}, \tag{5.13}$$

with

$$\begin{aligned} D_{ij} &= \int \mathrm{d}^3r' \Big\{ v_{xc}(\mathbf{r}')\Phi_j^\dagger(\mathbf{r}')\Phi_i(\mathbf{r}') \\ &+ \frac{1}{2ic}\mathbf{A}_{xc}(\mathbf{r}')\left[\Phi_j^\dagger(\mathbf{r}')\nabla'\Phi_i(\mathbf{r}') - \left(\nabla'\Phi_j^\dagger(\mathbf{r}')\right)\Phi_i(\mathbf{r}')\right] \\ &+ \mu_B\mathbf{B}_{xc}(\mathbf{r}')\Phi_j^\dagger(\mathbf{r}')\mathbf{sigma}\Phi_i(\mathbf{r}') - \Phi_j^\dagger(\mathbf{r}')\frac{\delta E_{xc}}{\delta\Phi_i^\dagger(\mathbf{r}')}\Big\}. \end{aligned} \tag{5.14}$$

The name "orbital shifts" (5.13) derives from their structure as a first-order shift from the unperturbed Kohn-Sham orbital $\Phi_i$ under a perturbation whose matrix elements are given by $D_{ij}$. The OEP equations (5.10)-(5.12) have a very simple interpretation: they merely say that the densities do not change under this perturbation.

In analogy to Sec. 3.2, we mention that the same equations may also be derived by minimizing the total energy with respect to the local effective fields.

At last, in connection with the nonuniqueness problem discussed in Sec. 4.4.1, the possibility of finding several sets of potentials producing the same set of densities may allow variations of the potentials for which the density response vanishes. If necessary, and as we will see in Sec. 5.2, supplementary conditions based, for example, on known properties for the potentials, can be considered to select one solution.

### 5.1.1 Practical solution of the OEP equations

By re-organizing the terms, the OEP equations can be rewritten as follows

$$R_v(\mathbf{r}) = \sum_k^{\text{occ}} \sum_j^{\text{un}} D_{kj} \frac{n_{kj}(\mathbf{r})}{\varepsilon_k - \varepsilon_j} + h.c. = 0, \tag{5.15}$$

$$R_{\mathbf{B}}(\mathbf{r}) = \sum_k^{\text{occ}} \sum_j^{\text{un}} D_{kj} \frac{\mathbf{m}_{kj}(\mathbf{r})}{\varepsilon_k - \varepsilon_j} + h.c. = 0 \ , \tag{5.16}$$

and

$$R_{\mathbf{A}}(\mathbf{r}) = \sum_k^{\text{occ}} \sum_j^{\text{un}} D_{kj} \frac{\mathbf{j}_{\mathbf{p}kj}(\mathbf{r})}{\varepsilon_k - \varepsilon_j} + h.c. = 0 \ , \tag{5.17}$$

where the first sum is carried over the occupied and the second one over the unoccupied orbitals. Here we have defined

$$\begin{aligned} n_{kj}(\mathbf{r}) &= \Phi_j^\dagger(\mathbf{r})\Phi_k(\mathbf{r}), & (5.18)\\ \mathbf{m}_{kj}(\mathbf{r}) &= -\mu_B \Phi_j^\dagger(\mathbf{r})\boldsymbol{\sigma}\Phi_k(\mathbf{r}), & (5.19)\\ \mathbf{j}_{\mathbf{p}kj}(\mathbf{r}) &= \frac{1}{2i}\left\{\Phi_j^\dagger(\mathbf{r})\nabla\Phi_k(\mathbf{r}) - \left[\nabla\Phi_j^\dagger(\mathbf{r})\right]\Phi_k(\mathbf{r})\right\}. & (5.20) \end{aligned}$$

Also $D_{kj}$ can be re-expressed as

$$\begin{aligned} D_{kj} &= \int \mathrm{d}^3 r' \Big\{ v_{xc}(\mathbf{r}')n_{kj}(\mathbf{r}') + \frac{1}{c}\mathbf{A}_{xc}(\mathbf{r}')\mathbf{j}_{\mathbf{p}kj}(\mathbf{r}') - \mathbf{B}_{xc}(\mathbf{r}')\mathbf{m}_{kj}(\mathbf{r}') \\ &- \Phi_j^\dagger(\mathbf{r}')\frac{\delta E_{xc}}{\delta\Phi_k^\dagger(\mathbf{r}')}\Big\}. \end{aligned} \tag{5.21}$$

This way of rewriting the equations is important because it suggests a practical scheme for the solution of the OEP equations. To this end, we observe that $R_v$, $R_{\mathbf{B}}$,

and $R_{\mathbf{A}}$ define three independent residues, which vanish when the correct orbitals and fields are plugged in. Hence, we expect that along the self-consistency cycle, the exchange-correlation potential residues will converge to zero. This leads to the idea to use the residues for updating the exchange-correlation fields as following

$$v_{xc}^{i}(\mathbf{r}) = v_{xc}^{i-1}(\mathbf{r}) - \alpha R_{v}^{i}(\mathbf{r}), \tag{5.22}$$

$$\mathbf{B}_{xc}^{i}(\mathbf{r}) = \mathbf{B}_{xc}^{i-1}(\mathbf{r}) - \alpha R_{\mathbf{B}}^{i}(\mathbf{r}), \tag{5.23}$$

and

$$\mathbf{A}_{xc}^{i}(\mathbf{r}) = \mathbf{A}_{xc}^{i-1}(\mathbf{r}) - \alpha R_{\mathbf{A}}^{i}(\mathbf{r}). \tag{5.24}$$

Here, $i$ refers to the number of iterations along the self-consistent cycle, and $\alpha$ is a mixing parameter chosen in order to speed up the convergence.

The only disadvantage of the above scheme may be in the explicit use of unoccupied levels. The scheme was first proposed in the SDFT context [69], and then extended by us to CSDFT. Experience has shown very good performance, especially when applied to extended systems.

For finite systems, it is well known that the KLI approximation - discussed in Chap. 3 - often performs extremely well. It is then appealing to extend this approximation to the non-collinear OEP equations in CSDFT. This is the topic of the following section.

### 5.1.2 KLI approximation in CSDFT

In this section, we suggest a simplifying approximation [43] in the spirit of Krieger, Li, and Iafrate (KLI) [45, 46] who introduced an analogous approximation in the (collinear) OEP method of (S)DFT (see Chap. 3). We then introduce the KLI procedure in CSDFT by approximating the orbital shifts as follows [68]

$$\Psi_i(\mathbf{r}) \approx \frac{1}{\Delta}\left[\sum_{j=1}^{\infty}\Phi_j(\mathbf{r})D_{ij} - \Phi_i(\mathbf{r})D_{ii}\right] , \tag{5.25}$$

where $\Delta$ is a constant. The value of $\Delta$ is not important since it drops out from the final expressions. Inserting this approximation into the OEP equations and applying the completeness relation for the Kohn-Sham spinors one obtains a set of algebraic equations for the exchange-correlation potentials which can conveniently be written as

$$\mathcal{D}(\mathbf{r})\mathcal{V}_{xc}(\mathbf{r}) = \mathcal{R}(\mathbf{r}) . \tag{5.26}$$

Here, we have defined the 7-component vector $\mathcal{V}_{xc}(\mathbf{r})$ as

$$\mathcal{V}_{xc}^{T}(\mathbf{r}) = \left(v_{xc}(\mathbf{r}), \mathbf{B}_{xc}^{T}(\mathbf{r}), \frac{1}{c}\mathbf{A}_{xc}^{T}(\mathbf{r})\right) , \tag{5.27}$$

and the $7 \times 7$ matrix $\mathcal{D}(\mathbf{r})$ has the structure

$$\mathcal{D}(\mathbf{r}) = \begin{pmatrix} n(\mathbf{r}) & -\mathbf{m}^T(\mathbf{r}) & \mathbf{j}_p^T(\mathbf{r}) \\ -\mathbf{m}(\mathbf{r}) & \mu_B^2 n(\mathbf{r}) \mathbb{1} & \mathcal{J}(\mathbf{r}) \\ \mathbf{j}_p(\mathbf{r}) & \mathcal{J}^T(\mathbf{r}) & \mathcal{N}(\mathbf{r}) \end{pmatrix} ,$$

where $\mathbb{1}$ is a $3 \times 3$ unit matrix. The matrix elements of the $3 \times 3$ matrices $\mathcal{J}$ and $\mathcal{N}$ are defined by

$$\mathcal{J}_{\alpha\beta}(\mathbf{r}) = -\frac{\mu_B}{2i} \sum_{i=1}^{N} \left[ \Phi_i^\dagger(\mathbf{r}) \sigma_\alpha \frac{\partial \Phi_i(\mathbf{r})}{\partial r_\beta} - \frac{\partial \Phi_i^\dagger(\mathbf{r})}{\partial r_\beta} \sigma_\alpha \Phi_i(\mathbf{r}) \right], \tag{5.28}$$

and

$$\begin{aligned} \mathcal{N}_{\alpha\beta}(\mathbf{r}) &= \frac{1}{2} \sum_{i=1}^{N} \left[ \frac{\partial \Phi_i^\dagger(\mathbf{r})}{\partial r_\alpha} \frac{\partial \Phi_i(\mathbf{r})}{\partial r_\beta} + \frac{\partial \Phi_i^\dagger(\mathbf{r})}{\partial r_\beta} \frac{\partial \Phi_i(\mathbf{r})}{\partial r_\alpha} \right] \\ &\quad - \frac{1}{4n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial r_\alpha} \frac{\partial n(\mathbf{r})}{\partial r_\beta} , \end{aligned} \tag{5.29}$$

where $\alpha = 1, 2, 3$ corresponds to the cartesian coordinates $x$, $y$, and $z$, respectively. The seven components of the vector $\mathcal{R}(\mathbf{r})$ on the right-hand side of Eq. (5.26) are given by

$$\mathcal{R}_1(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{N} \left[ \Phi_i^\dagger(\mathbf{r}) \frac{\delta E_{xc}}{\delta \Phi_i^\dagger(\mathbf{r})} + n_i(\mathbf{r}) D_{ii} + h.c. \right], \tag{5.30}$$

$$\mathcal{R}_{1+\alpha}(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{N} \left[ -\mu_B \Phi_i^\dagger(\mathbf{r}) \sigma_\alpha \frac{\delta E_{xc}}{\delta \Phi_i^\dagger(\mathbf{r})} + m_{i,\alpha}(\mathbf{r}) D_{ii} + h.c. \right] ,$$

$$\mathcal{R}_{4+\alpha}(\mathbf{r}) = \frac{1}{2} \sum_{k=1}^{N} \left[ \frac{1}{2i} \Phi_k^\dagger(\mathbf{r}) \frac{\partial}{\partial r_\alpha} \frac{\delta E_{xc}}{\delta \Phi_k^\dagger(\mathbf{r})} - \frac{1}{2i} \frac{\partial \Phi_k^\dagger(\mathbf{r})}{\partial r_\alpha} \frac{\delta E_{xc}}{\delta \Phi_k^\dagger(\mathbf{r})} + j_{p,k,\alpha}(\mathbf{r}) D_{kk} + h.c. \right] \tag{5.31}$$

with the density $n_i(\mathbf{r})$, magnetization density $\mathbf{m}_i(\mathbf{r})$, and paramagnetic current density $\mathbf{j}_{p,i}(\mathbf{r})$ of the single orbital $\Phi_i(\mathbf{r})$. It is worth mentioning that in order to arrive at this result we used the identity (4.56), which follows directly from the gauge invariance of the exchange-correlation energy.

The KLI equations (5.26) can be solved by iteration: start with an intial guess for the potentials to compute the orbitals and the right-hand side of Eq. (5.26), then solve this equation for the new potentials and iterate until self-consistency is achieved. Again, in connection with the nonuniqueness problem, discussed in Sec. 4.4.1, the possibility of finding several sets of potentials producing the same set of densities may require to specify a solution by using supplementary conditions as, for example, is done in the Sec. 5.2.

## 5.2 CSDFT-KLI potentials for open-shell atoms

In order to gain some intuition in the KLI equations of CSDFT, we will now analyze the case of atoms at vanishing external magnetic field in more detail [68]. This analysis is also useful as an introduction to the next chapter dealing with the degeneracy problem for open-shell atoms. In the case of zero external magnetic field, the Kohn-Sham equation takes the form

$$\left[-\frac{\nabla^2}{2}+v(\mathbf{r})+v_H(\mathbf{r})+v_{xc}(\mathbf{r})+\frac{1}{2ic}\nabla\mathbf{A}_{xc}(\mathbf{r})+\frac{1}{ic}\mathbf{A}_{xc}(\mathbf{r})\nabla+\mu_B\boldsymbol{\sigma}\mathbf{B}_{xc}(\mathbf{r})\right]\Phi_i(\mathbf{r})=\epsilon_i\Phi_i(\mathbf{r})\ . \tag{5.32}$$

In the following, as we have done in Sec. 4.1.1, we employ the collinear approximation. In addition, we assume cylindrical symmetry for both the densities and the corresponding conjugate potentials (i. e., they do not depend on the azimuthal angle $\phi$). As a consequence the magnetic quantum number is a good quantum number for the single-particle orbitals which then take the form

$$\varphi_{im\sigma}(\mathbf{r}) = g_{i\sigma}(r,\theta)\exp(im\phi)\chi(\sigma)\ , \tag{5.33}$$

where we used spherical coordinates and $m$ is the magnetic quantum number (not to be confused with $m(\mathbf{r})$, the $z$-component of the magnetization density). $\sigma$ is the spin index and $\chi(\sigma)$ is the eigenfunction of the $z$-component of the spin operator. Thus, $\sigma = +1$ for spin-up, and $\sigma = -1$ for spin-down. In the collinear approximation, $\mathbf{B}_{xc}(\mathbf{r}) = (0,0,B_{xc}(\mathbf{r}))$ is parallel to the $z$-axis while $\mathbf{A}_{xc}(\mathbf{r}) = A_{xc}(\mathbf{r})\mathbf{e}_\phi$ where $\mathbf{e}_\phi$ is the unit vector in $\phi$-direction. As an additional consequence of the cylindrical symmetry of our problem we have $\nabla\mathbf{A}_{xc}(\mathbf{r}) = 0$.

We restrict ourselves to ground states whose densities can be reproduced by a single Slater determinant. For example, for the boron atom one configuration has all three up-electrons and the two down-electrons in states with magnetic quantum number $m = 0$ while in another configuration one of the up-electrons occupies an $m = 1$ state with the other occupations unchanged. In this way current-carrying and zero-current states can be considered. The resulting current only has a component in the $\phi$-direction, $\mathbf{j}_p(\mathbf{r}) = j_p(\mathbf{r})\mathbf{e}_\phi$. We may then rewrite Eq. (5.32) as

$$\left[-\frac{\nabla^2}{2}+v(\mathbf{r})+v_H(\mathbf{r})+v_{xc}(\mathbf{r})+\frac{1}{c}\frac{m}{r\sin\theta}A_{xc}(\mathbf{r})+\mu_B\sigma B_{xc}(\mathbf{r})\right]\varphi_{im\sigma}(\mathbf{r}) = \epsilon_{im\sigma}\varphi_{im\sigma}(\mathbf{r})\ . \tag{5.34}$$

We now discuss a number of typical cases: For atomic closed-shell configurations, where the density is spherical and both the magnetization density and the paramagnetic current density vanish identically, both $A_{xc}$ and $B_{xc}$ vanish identically. Obviously, in this situation CSDFT reduces to the original DFT.

For ground state configurations where only orbitals with $m = 0$ are occupied, the correct value for $j_p(\mathbf{r})$ – which is zero at any point in space – is trivially obtained already within the SDFT scheme. Therefore we expect that $v_{xc}(\mathbf{r}) = v_{xc}^{\mathrm{SDFT}}(\mathbf{r})$, $B_{xc}(\mathbf{r}) = B_{xc}^{\mathrm{SDFT}}(\mathbf{r})$, and $A_{xc}(\mathbf{r}) = 0$. Actually, any other choice of $A_{xc}(\mathbf{r})$ would not

make any difference for the ground state densities (because of the prefactor $m = 0$ in Eq. (5.34)). In a way this may be regarded as a simple manifestation of the non-uniqueness of the CSDFT potentials pointed out in Ref. [62].

As a third case we consider ground state configurations with a half-filled shell as, e.g., in the nitrogen atom. Again, SDFT already gives the correct values of the total densities. Therefore, we again expect that $v_{xc}(\mathbf{r}) = v_{xc}^{\mathrm{SDFT}}(\mathbf{r})$, $B_{xc}(\mathbf{r}) = B_{xc}^{\mathrm{SDFT}}(\mathbf{r})$, and $A_{xc}(\mathbf{r}) = 0$.

Ground state configurations carrying a non-vanishing paramagnetic current are the most interesting ones in our context. At zero external magnetic field, this situation only arises for open-shell atoms away from half-filling. Indeed, it is for these states that we expect $A_{xc}(\mathbf{r}) \neq 0$ as well as $v_{xc}(\mathbf{r}) \neq v_{xc}^{\mathrm{SDFT}}(\mathbf{r})$, $B_{xc}(\mathbf{r}) \neq B_{xc}^{\mathrm{SDFT}}(\mathbf{r})$.

In the following we analyze the KLI equations for the above cases in order to confirm these expectations. We remind the reader that in our derivation of the OEP equations we assumed that $E_{xc}$ depends only on the occupied orbitals. As a consequence

$$\frac{\delta E_{xc}}{\delta \varphi_{im\sigma}(\mathbf{r})} \sim \exp(-im\phi) \tag{5.35}$$

holds. In this case, the first two KLI equations are

$$v_{xc,\sigma}(\mathbf{r}) + \frac{1}{c}\frac{j_{p,\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})} A_{xc}(\mathbf{r}) = w_{xc,\sigma}^{(1)}(\mathbf{r}) + w_{xc,\sigma}^{(2)}(\mathbf{r}) \ , \tag{5.36}$$

where we have defined the spin-dependent scalar potential

$$v_{xc,\sigma}(\mathbf{r}) = v_{xc}(\mathbf{r}) + \mu_B \sigma B_{xc}(\mathbf{r}). \tag{5.37}$$

The terms on the right-hand side of Eq. (5.36) are given by

$$w_{xc,\sigma}^{(1)}(\mathbf{r}) = \frac{1}{n_\sigma(\mathbf{r})} \sum_{i,m}^{\mathrm{occ}} n_{im\sigma}(\mathbf{r}) u_{xc,im\sigma}(\mathbf{r}) \ , \tag{5.38}$$

$$w_{xc,\sigma}^{(2)}(\mathbf{r}) = \frac{1}{n_\sigma(\mathbf{r})} \sum_{i,m}^{\mathrm{occ}} n_{im\sigma}(\mathbf{r}) d_{xc,im\sigma} \tag{5.39}$$

with

$$u_{xc,im\sigma}(\mathbf{r}) = \frac{1}{\varphi_{im\sigma}^*(\mathbf{r})} \frac{\delta E_{xc}}{\delta \varphi_{im\sigma}(\mathbf{r})} \ , \tag{5.40}$$

and

$$d_{xc,im\sigma} = \int \mathrm{d}^3 r \ n_{im\sigma}(\mathbf{r}) \left[ v_{xc,\sigma}(\mathbf{r}) - u_{xc,im\sigma}(\mathbf{r}) \right] + \frac{1}{c} \int \mathrm{d}^3 r \ j_{p,im\sigma}(\mathbf{r}) A_{xc}(\mathbf{r}) \ . \tag{5.41}$$

Here $n_{im\sigma}(\mathbf{r})$ and $j_{p,im\sigma}(\mathbf{r})$ are the density and the paramagnetic current density of the single orbital $\varphi_{im\sigma}(\mathbf{r})$ which, for our symmetry, are related by

$$j_{p,im\sigma}(\mathbf{r}) = m \ \frac{n_{im\sigma}(\mathbf{r})}{r \sin\theta} \ . \tag{5.42}$$

The third KLI equation reads

$$\sum_\sigma j_{p,\sigma}(\mathbf{r}) v_{xc,\sigma}(\mathbf{r}) + \frac{1}{c} N(\mathbf{r}) A_{xc}(\mathbf{r}) = \sum_\sigma \left[ \tilde{w}^{(1)}_{xc,\sigma}(\mathbf{r}) + \tilde{w}^{(2)}_{xc,\sigma}(\mathbf{r}) \right] \tag{5.43}$$

with

$$N(\mathbf{r}) = \sum_\sigma \sum_{i,m}^{\text{occ}} \frac{j^2_{p,im\sigma}(\mathbf{r})}{n_{im\sigma}(\mathbf{r})} \ , \tag{5.44}$$

$$\tilde{w}^{(1)}_{xc,\sigma}(\mathbf{r}) = \sum_{i,m}^{\text{occ}} j_{p,im\sigma}(\mathbf{r}) u_{xc,im\sigma}(\mathbf{r}) \ , \tag{5.45}$$

and

$$\tilde{w}^{(2)}_{xc,\sigma}(\mathbf{r}) = \sum_{i,m}^{\text{occ}} j_{p,im\sigma}(\mathbf{r}) d_{xc,im\sigma} \ . \tag{5.46}$$

It is interesting to note that $v_{xc,\sigma}(\mathbf{r})$ and $A_{xc}(\mathbf{r})$ couple to each other only if at least one $j_{p,\sigma}(\mathbf{r})$ is non-vanishing.

At this point, we first consider open-shell configurations for which all occupied orbitals have $m = 0$. Then $N(\mathbf{r})$ vanishes and the KLI equation (5.36) reduces to the KLI equation of SDFT, while Eq. (5.43) becomes a trivial identity. As a consequence, $v_{xc,\sigma}(\mathbf{r}) = v^{\text{SDFT}}_{xc,\sigma}(\mathbf{r})$ and $A_{xc}(\mathbf{r})$ is undetermined. As discussed above, $A_{xc}(\mathbf{r})$ does not affect any of the ground state densities and hence we fix $A_{xc}(\mathbf{r}) = 0$.

Next we consider configurations with a half-filled shell. We assume that we have already solved the SDFT-KLI equations and use the resulting orbitals and potentials plus the initial guess $A_{xc}(\mathbf{r}) = 0$ as a start for the iterative solution of the CSDFT-KLI equations. We substitute this initial guess into Eqs. (5.36) and (5.43) to compute the new potentials. The occupied orbitals of SDFT either have $m = 0$ or they come in pairs with $m$ and $-m$. This leads to the same contributions to $u_{xc,\sigma,i}(\mathbf{r})$ for orbitals in the same shell, while for the paramagnetic current they contribute with equal magnitude but opposite sign. Hence, the KLI equations become

$$v^{\text{new}}_{xc,\sigma}(\mathbf{r}) = w^{(1)}_{xc,\sigma}(\mathbf{r}) + w^{(2)}_{xc,\sigma}(\mathbf{r}) = v^{\text{SDFT}}_{xc,\sigma}(\mathbf{r}) \tag{5.47}$$

and

$$\frac{1}{c} N(\mathbf{r}) A^{\text{new}}_{xc}(\mathbf{r}) = 0 \Rightarrow A^{\text{new}}_{xc}(\mathbf{r}) = 0 \ . \tag{5.48}$$

This shows that the SDFT solution along with $A_{xc}(\mathbf{r}) = 0$ is also a CSDFT solution. We also tested numerically that the solution $A_{xc}(\mathbf{r}) = 0$ is stable against (not necessarily small) perturbations of the initial guess.

Finally, we consider the most interesting case of ground state configurations with a paramagnetic current different from zero. For these configurations we expect $A_{xc}(\mathbf{r}) \neq 0$. Solution of the third KLI-equation (5.43) with respect to $A_{xc}(\mathbf{r})$ yields

$$A_{xc}(\mathbf{r}) = c \, \frac{\sum_\sigma \left[ \tilde{w}^{(1)}_{xc,\sigma}(\mathbf{r}) + \tilde{w}^{(2)}_{xc,\sigma}(\mathbf{r}) - j_{p,\sigma}(\mathbf{r}) v_{xc,\sigma}(\mathbf{r}) \right]}{N(\mathbf{r})} \ . \tag{5.49}$$

In this equation, the denominator increases with increasing number of electrons. The numerator also typically increases when more orbitals are occupied but, due to large cancellations for contributions arising from orbitals with opposite values of $m$, it increases with a slower rate than the denominator. As a consequence, we expect larger exchange-correlation vector potentials $A_{xc}(\mathbf{r})$ for atoms in the first row than for atoms in the second row (but the same column) of the periodic table.

In the remainder of this section we discuss the asymptotic behavior of the exchange-correlation potentials and the vector potential.

We start by *assuming* that, for finite systems, the exchange-correlation potentials in the asymptotic region far away from the system behave as

$$v_{xc,\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} -\frac{1}{r} \tag{5.50}$$

and

$$\lim_{r\to\infty} A_{xc}(\mathbf{r}) = 0 \; . \tag{5.51}$$

Eq. (5.50) certainly is a reasonable assumption: it is the well-known asymptotic behavior for $v_{xc,\sigma}$ of SDFT which we assume to be unchanged in CSDFT. Eq. (5.51) then ensures that the term proportional to $A_{xc}(\mathbf{r})/r$ in the Kohn-Sham equation (5.34) decays faster than $v_{xc,\sigma}(\mathbf{r})$ asymptotically. At this stage, Eq. (5.51) may be viewed as a working assumption in order to be able to proceed further. Below we show that it is consistent with the solution of the KLI equation.

Under this assumption we can deduce [70, 38] the asymptotic behavior of the atomic orbitals from the Kohn-Sham equation (5.34) as

$$\lim_{r\to\infty} \varphi_{im\sigma}(\mathbf{r}) = r^{-1+1/\beta_{im\sigma}} \exp(-\beta_{im\sigma} r) \; , \tag{5.52}$$

where $\beta_{im\sigma} = \sqrt{-2\epsilon_{im\sigma}}$. This implies that the spin density is dominated asymptotically by the highest occupied orbital of that spin. The same is true for the current density if the magnetic quantum number of this orbital is different from zero (as is the case for current-carrying states of open-shell atoms).

In order to proceed further with our analysis we restrict ourselves to the exact-exchange functional of Eq. (5.4). Then the KLI equation (5.36) allows us to establish the following relation between $v_{xc,\sigma}$ and $A_{xc}$ in the asymptotic region

$$\lim_{r\to\infty} v_{xc,\sigma}(\mathbf{r}) + \frac{1}{c}\frac{M_\sigma}{r\sin\theta} A_{xc}(\mathbf{r}) \to -\frac{1}{r} + d_{xc,N_\sigma M_\sigma \sigma} \; , \tag{5.53}$$

where we tacitly assumed that we are taking the limit away from a nodal plane of the highest occupied orbital of spin $\sigma$ [38, 48]. Here $N_\sigma$ is the orbital index of that orbital and $M_\sigma$ is its magnetic quantum number. Since we are working in the collinear approximation, the Kohn-Sham equations for the two spin channels are completely decoupled and we can choose a constant shift in $v_{xc,\sigma}$ such that

$$d_{xc,N_\sigma M_\sigma \sigma} = 0 \; . \tag{5.54}$$

Eq. (5.53) together with Eq. (5.50) then implies

$$\frac{M_\sigma}{r\sin\theta}A_{xc}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} 0 \tag{5.55}$$

which is consistent with the assumption of Eq. (5.51).

However, a closer inspection of the KLI equations (5.36) and (5.43) shows that they become linearly dependent in the asymptotic region and therefore do not have a unique solution. This again may be viewed as a manifestation of the non-uniqueness problem in CSDFT [61, 62]. In our numerical procedure to be described in the next chapter, we take a pragmatic approach to the problem of linearly dependent KLI equations and choose a solution with $A_{xc}(\mathbf{r}) \to 0$ and a $v_{xc,\sigma}(\mathbf{r})$ satisfying Eq. (5.50). This procedure enforces a unique solution in the cases studied.

### 5.2.1 Physical versus effective magnetic fields

We have just observed above that for spin-polarized but zero-current states, $\mathbf{A}_{xc} = 0$ and $\mathbf{B}_{xc} \neq 0$ is a solution. We can then consider the case where both $\mathbf{A}_{xc}$ and $\mathbf{B}_{xc}$ are different from zero. By inspection of the two KLI-equations (5.36) and (5.43) it is clear that under the exchange of spin-up and spin-down electrons, $\mathbf{B}_{xc}(\mathbf{r})$ changes sign. Similarly, exchanging an electron from an orbital with magnetic quantum number $m$ to a previously unoccupied one with $-m$ leads to $\mathbf{A}_{xc}(\mathbf{r})$ changing sign. These transformations can be performed independently leading to the same total energy. Hence, the relative sign of $\mathbf{A}_{xc}$ and $\mathbf{B}_{xc}$ can change independently, that would not be the case if $\mathbf{B}_{xc} = \nabla \times \mathbf{A}_{xc}$.

As we have seen in Sec. 4.5, if one insists on defining the effective magnetic field in terms of the effective vector potential then one has to resort to $\mathbf{j}_m$-DFT. One might wonder how the OEP equations would look in the latter formulation. The answer is given in the next section.

## 5.3 OEP equations for $\mathbf{j}_m$-DFT

In working out the expressions of the $\mathbf{j}_m$-OEP equations, one has to consider only external and exchange-correlation magnetic fields that are given as curl of the external and exchange-correlation vector potential, respectively. Therefore, the possible variations are also related by $\delta\mathbf{B}_s = \nabla\times\delta\mathbf{A}_s$. In addition, in this case one has to use that the exchange-correlation energy functional depends, through the Kohn-Sham spinors, on the basic densities $(n, \mathbf{j}_m)$. Then, one may start by writing the following identites

$$\begin{aligned}\frac{\delta E_{xc}}{\delta v_s(\mathbf{r})} &= \int \mathrm{d}^3r' \left[ v_{xc}(\mathbf{r}')\frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \frac{1}{c}\mathbf{A}_{xc}(\mathbf{r}')\frac{\delta \mathbf{j}_m(\mathbf{r}')}{\delta v_s(\mathbf{r})}\right] \\ &= \sum_{k=1}^{N}\int \mathrm{d}^3r' \left[ \frac{\delta E_{xc}}{\delta\Phi_k(\mathbf{r}')}\frac{\delta\Phi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} + h.c.\right]\end{aligned} \tag{5.56}$$

$$\frac{\delta E_{xc}}{\delta \mathbf{A}_s(\mathbf{r})} = \int \mathrm{d}^3 r' \left[ v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} + \frac{1}{c} \mathbf{A}_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_m(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} \right]$$
$$= \sum_{k=1}^{N} \int \mathrm{d}^3 r' \left[ \frac{\delta E_{xc}}{\delta \Phi_k(\mathbf{r}')} \frac{\delta \Phi_k(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} + h.c. \right] . \quad (5.57)$$

However, here we prefer to arrive at the final (exact) expressions of these equations along a somewhat simplistic but meaningful derivation.

Let us consider again the CSDFT-OEP equations given in Eqs. (5.10), (5.11) and (5.12). Note that Eq. (5.10) is a statement for the particle density, so it does not need to be changed. The second and the third ones instead are conditions for the magnetization and paramagnetic-current densities. We can thus combine them in the fashion as $\mathbf{j}_p$ and $\mathbf{m}$ are combined in $\mathbf{j}_m$. The resulting equations are

$$\sum_{i=1}^{N} \Phi_i^\dagger(\mathbf{r}) \Psi_i(\mathbf{r}) + h.c. = 0, \quad (5.58)$$

and

$$\frac{1}{2i} \sum_{i=1}^{N} \left\{ \Phi_i^\dagger(\mathbf{r}) \nabla \Psi_i(\mathbf{r}) - \left[ \nabla \Phi_i^\dagger(\mathbf{r}) \right] \Psi_i(\mathbf{r}) \right\} + \frac{1}{2} \nabla \times \left\{ \sum_{i=1}^{N} \Phi_i^\dagger(\mathbf{r}) \boldsymbol{\sigma} \Psi_i(\mathbf{r}) \right\} + h.c. = 0 \, . \quad (5.59)$$

Also, we need not reconsider the definition of the orbital shifts $\Psi_i(\mathbf{r})$.

In fact, note that the definition of $D_{ij}$ in Eq. (5.14) contains the $\mathbf{B}_{xc}$ filed. Here we have to insert the "restriction" $\mathbf{B}_{xc} = \nabla \times \mathbf{A}_{xc}$. Then, we may integrate by parts (assuming vanishing surface contributions). This leads to

$$D_{ij} = \int \mathrm{d}^3 r' \Bigg\{ v_{xc}(\mathbf{r}') \Phi_j^\dagger(\mathbf{r}') \Phi_i(\mathbf{r}') + \frac{1}{2ic} \mathbf{A}_{xc}(\mathbf{r}') \left[ \Phi_j^\dagger(\mathbf{r}') \nabla' \Phi_i(\mathbf{r}') - \left( \nabla' \Phi_j^\dagger(\mathbf{r}') \right) \Phi_i(\mathbf{r}') \right]$$
$$+ \frac{1}{2c} \mathbf{A}_{xc}(\mathbf{r}') \nabla \times \left[ \Phi_j^\dagger(\mathbf{r}') \boldsymbol{\sigma} \Phi_i(\mathbf{r}') \right] - \Phi_j^\dagger(\mathbf{r}') \frac{\delta E_{xc}}{\delta \Phi_i^\dagger(\mathbf{r}')} \Bigg\}. \quad (5.60)$$

In summary, we have obtained two coupled equations which provide $v_{xc}$ and $\mathbf{A}_{xc}$. This is all what is needed since, as should be clear by now, $\mathbf{B}_{xc}$ is obtained directly from $\mathbf{A}_{xc}$.

Before concluding, we analyze the consequence of the collinear approximation, and the assumption of cylindrical symmetry for the densities and potentials. Because of these restrictions and $\mathbf{B}_s$ being source free (this follows from the fact that $\mathbf{B}_s$ is a curl of a vector), we obtain the condition

$$\nabla \cdot \mathbf{B}_s(\mathbf{r}) = \frac{\partial}{\partial z} B_z(\rho, z) = 0, \quad (5.61)$$

where $\rho$ and $z$ are cylindrical coordinates. In other words, the only non-vanishing component of this field may vary only with respect to $\rho$. It is apparent that this field is quite different from the one usually computed in the standard LSDA and LVA. Further analysis of OEP-$\mathbf{j}_m$ equations is subject of an ongoing work.

## 5.4 Non-collinear OEP method in SDFT

For studying systems exhibiting non-collinear magnetism, SDFT is commonly applied under the assumption of local collinearity, i.e., the Kohn-Sham magnetic field is assumed to be locally parallel to the magnetization vector [71]. This is necessary since the electron-gas based approximations for the functionals assume a collinear state for the electron gas. The OEP method has been originally introduced in SDFT for the case of *global* collinearity. In this case, the magnetization and the total Kohn-Sham magnetic field are assumed to have the same direction everywhere in space. In this restricted case, as we have seen in Sec. 4.1.1, one needs only to consider two "separate" problems: one for the spin up, and the other for the spin down orbitals. A rigorous non-collinear description is immediately obtained if one accepts to employ exchange-correlation functionals which explicitly depend on two-component Kohn-Sham spinors - without further restricting their form.

Having in mind the differences between the SDFT and CSDFT, and starting with the OEP equations for CSDFT (Eqs. (5.10), (5.11) and (5.12)), the corresponding ones for SDFT may be obtained by neglecting the coupling to the external vector potential, and thus neglecting the dependence on the paramagnetic current in the functionals. Thus, the third equation (5.12) has to be ignored - since, it is merely a statement on the paramagnetic-current density (which comes from the possibility of varying with respect the vector potential). Still we need the two first equations, which we rewrite as

$$\sum_{k=1}^{N} \Phi_k^\dagger(\mathbf{r})\Psi_k(\mathbf{r}) + h.c. = 0 \tag{5.62}$$

and

$$-\mu_B \sum_{k=1}^{N} \Phi_k^\dagger(\mathbf{r})\boldsymbol{\sigma}\Psi_k(\mathbf{r}) + h.c. = 0. \tag{5.63}$$

Here we must not forget to remove the vector potential and currents from the definition of the orbital shifts $\Phi_k^\dagger(\mathbf{r})$. This is carried out by rewriting

$$D_{kj} = \int \mathrm{d}^3 r' \left\{ \Phi_j^\dagger(\mathbf{r}') \Big[ v_{xc}(\mathbf{r}') + \mu_B \boldsymbol{\sigma} \mathbf{B}_{xc}(\mathbf{r}') \Big] \Phi_k(\mathbf{r}') - \Phi_j^\dagger(\mathbf{r}') \frac{\delta E_{xc}}{\delta \Phi_k^\dagger(\mathbf{r}')} \right\} . \tag{5.64}$$

As we have shown in Ref. [22], the same equations can also be derived more pedantically proceeding similarly as we have done for the CSDFT-OEP equations. Alternatively as shown in Ref. [69], they can be derived by using the conditions for the minimum of the total energy as functional of the local effective fields.

Furthermore, along the lines of Sec. 3.4, we can give an exact transformation of the equations (5.62) and (5.63). This is carried out by considering the differential equation for the orbital shifts

$$\Big[ \hat{h}_s(\mathbf{r}) - \varepsilon_k \Big] \Psi_k(\mathbf{r}) = - \Big[ v_{xc}(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \mathbf{B}_{xc}(\mathbf{r}) \Big] \Phi_k(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \Phi_k^\dagger(\mathbf{r})} + D_{kk} \Phi_k(\mathbf{r}) \ , \tag{5.65}$$

which, together with the OEP equations (5.62) and (5.63), eventually leads to the transformed OEP equations for non-collinear spin-DFT. These may most conveniently be written in matrix notation as

$$\begin{pmatrix} n(\mathbf{r}) & -m_1(\mathbf{r}) & -m_2(\mathbf{r}) & -m_3(\mathbf{r}) \\ -m_1(\mathbf{r}) & \mu_B^2 n(\mathbf{r}) & 0 & 0 \\ -m_2(\mathbf{r}) & 0 & \mu_B^2 n(\mathbf{r}) & 0 \\ -m_3(\mathbf{r}) & 0 & 0 & \mu_B^2 n(\mathbf{r}) \end{pmatrix} \begin{pmatrix} v_{xc}(\mathbf{r}) \\ B_{xc,1}(\mathbf{r}) \\ B_{xc,2}(\mathbf{r}) \\ B_{xc,3}(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} g_1(\mathbf{r}) \\ g_2(\mathbf{r}) \\ g_3(\mathbf{r}) \\ g_4(\mathbf{r}) \end{pmatrix} \quad . \tag{5.66}$$

Here we have defined

$$g_1(\mathbf{r}) = \frac{1}{2} \sum_{k=1}^{N} \left\{ u_{xck}(\mathbf{r}) - \nabla \left[ \left( \nabla \Phi_k^\dagger(\mathbf{r}) \right) \Psi_k(\mathbf{r}) \right] + n_k(\mathbf{r}) D_{kk} + h.c. \right\} \tag{5.67}$$

with the orbital densities

$$n_k(\mathbf{r}) = \Phi_k^\dagger(\mathbf{r}) \Phi_k(\mathbf{r}) \tag{5.68}$$

and

$$u_{xck}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \Phi_k(\mathbf{r})} \Phi_k(\mathbf{r}) \ . \tag{5.69}$$

The other terms on the right-hand side of Eq. (4.26) are given by

$$g_{\alpha+1}(\mathbf{r}) = \frac{\mu_B}{2} \sum_{k=1}^{N} \left\{ \tilde{u}_{xck,\alpha}(\mathbf{r}) - \nabla \left[ \left( \nabla \Phi_k^\dagger(\mathbf{r}) \right) \sigma_\alpha \Psi_k(\mathbf{r}) \right] + m_{k,\alpha}(\mathbf{r}) D_{kk} + h.c. \right\} \tag{5.70}$$

with $\alpha = 1, 2, 3$ and the Pauli matrices $\sigma_1 = \sigma_x$ etc. as well as the orbital magnetization

$$m_{k,\alpha}(\mathbf{r}) = -\mu_B \Phi_k^\dagger(\mathbf{r}) \sigma_\alpha \Phi_k(\mathbf{r}) \tag{5.71}$$

and

$$\tilde{u}_{xck,\alpha}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \Phi_k(\mathbf{r})} \sigma_\alpha \Phi_k(\mathbf{r}) \ . \tag{5.72}$$

We recall that Gidopoulos has recently showed that the nonuniqueness problem does not affect SDFT on the class of ground states densities with non collinear magnetizations produced by external non-collinear magnetic fields [64].

# Chapter 6

# Open-shell atoms and the degeneracy problem

As we have discussed in chapter 2, the Hohenberg-Kohn [3] and Kohn-Sham [4] theorems of DFT, which were originally established for non-degenerate ground states, can be extended to degenerate ground states as well [5, 6]. These degenerate ground states lead to a set of different ground state densities, and the exact energy functional yields the same ground state energy for all these densities. It has long been known, however, that common approximations do not yield the same total energies [72, 73, 74, 75]. In a systematic investigation of this problem Baerends and coworkers [76] showed that for states with different total magnetic quantum number, $M_L$, spurious energy splittings of up to 5 kcal/mol result from generalized gradient approximations (GGA's). Splittings even up to 10 kcal/mol are observed for the meta-GGA's [77].

Recently, the problem has attracted renewed interest. Becke has proposed an approach for constructing exchange-correlation functionals with an increased ability to reproduce the degeneracy of atomic states [78]. The essential idea is to enforce the proper description of the Fermi (or exchange) hole curvature [79] in the approximation of the exchange-correlation energy functional [29]. As a consequence, the paramagnetic current density appears explicitly in the expression of the corresponding functional [80]. This improves the description of the atomic degeneracy [78] of states carrying different paramagnetic current densities.

Along the line of Becke's approach, Maximoff et al [81] have modified the GGA of Perdew, Burke, and Ernzerhof (PBE) to a form explicitly depending on the paramagnetic current density. In this way, they successfully reduced the previous spurious energy splittings. Actually, they have weakened Becke's suggestion by improving not the exchange hole curvature at all points in space, but rather its "system" average.

More recently, Tao and Perdew [77] have employed ideas of the current-DFT framework of Vignale and Rasolt [52]. They constructed a current-dependent correction to GGA and meta-GGA functionals and their results again suggest that some improvements for the energy splittings can be achieved.

Motivated by the observed importance of the exchange-hole curvature and its current terms, we here study the performance of the exact-exchange (EXX) energy functional which, by definition, describes the curvature correctly for the energy splittings in DFT, SDFT and CSDFT [68, 82, 83]. In our investigation, we will stay within the framework of orbital functionals, adopting the OEP method in different flavors of DFT. But as in all the previus investigations, we only consider densities represented by single Slater determinants of Kohn-Sham orbitals.

## 6.1 Energy splittings in exact-exchange approximation

In this section, we investigate the degeneracy problem for the atoms of the second and third row in the periodic table at the exact-exchange-only level in DFT, SDFT and CSDFT using the KLI approximation. These are the atoms which are also considered as reference cases in Refs. [77, 78, 81]. For heavier elements such as the transition metals, there are additional complications in the analysis of the degeneracy problem: physically, inclusion of spin-orbit coupling will be necessary to describe the ground states properly. But also for purely non-relativistic calculations the absolute error in total ground-state energies in the KLI approximation as compared to full OEP calculations in SDFT is typically a factor of three to five larger for the transition metals than for the lighter atoms [38]. Thus when considering transition metals we could never claim to reach the same accuracy that we achieved for the lighter elements.

### 6.1.1 Numerical implementation

Although the (interacting) Hamiltonian of an atom has spherical symmetry, the ground state densities of open-shell atoms typically are not spherical. However, for any of the possible degenerate ground states one can always find an axis for which the corresponding density exhibits cylindrical symmetry and we choose this axis as the $z$-axis of our coordinate system. We seek a Kohn-Sham single-particle potential with the same cylindrical symmetry. Then the magnetic quantum number $m$ is a good quantum number to characterize the Kohn-Sham orbitals. We can perform self-consistent calculations by specifying how many orbitals with $m = 0, 1, \ldots$ are occupied for each spin channel, and we then keep this configuration fixed throughout the self-consistency cycle. In this way the current-carrying and zero-current states can be considered.

Along these lines, we have developed an atomic code for DFT, SDFT and CSDFT calculations in a basis set representation, assuming cylindrical symmetry of the Kohn-Sham potential. As basis functions we use the Slater-type functions of Ref. [84] for the radial part, multiplied with spherical harmonics for the angular part. We then express the KS Hamiltonian matrix in this basis and by standard

matrix diagonalization obtain the KS orbitals as linear combinations of the basis functions.

We have tested our code by computing the total energies of spherically symmetric atoms of the first and second row of the periodic table in exchange-only KLI approximation and compared with results from accurate, fully numerical codes available in the literature [38, 45, 85]. Using the quadruple zeta basis sets (QZ4P) of Slater functions [84], our code reproduces these energies to within a maximum deviation of 0.3 kcal/mol and an average deviation of 0.1 kcal/mol for the first-row atoms and to within a maximum deviation of 0.9 kcal/mol and an average deviation of 0.5 kcal/mol for the second row. As an additional estimate of the accuracy of our calculations we have also computed the energy splittings between different configurations in LSDA. Our results reproduce the spurious energy splittings reported in Ref. [78] with a deviation of less than 0.02 kcal/mol. As a combination of these error estimates we expect our result for spurious energy splittings to be accurate at least at a level of about 0.1 kcal/mol.

### 6.1.2 Results for DFT and SDFT

We have calculated self-consistent total energies for different configurations of open-shell atoms. Tab. 7.1 shows the energy differences (spurious energy splittings) between Kohn-Sham Slater determinants with *total* magnetic quantum number $|M| = 1$ and $M = 0$ in kcal/mol. For comparison we also list the results of the current-dependent exchange-only functionals of Refs. [78] (denoted jBR) and [81] (denoted jPBE) in the first and second columns, respectively. Our SDFT results for the exact-exchange functional lead to larger splittings than both the jBR and the jPBE functionals. The idea behind the construction of these functionals is to improve the exchange-hole curvature by inclusion of the orbital paramagnetic current density. Since in our calculations we have used the exact exchange functional (and therefore also the correct exchange hole curvature), the success of the jBR and jPBE functionals in reducing the energy splittings might actually be due to an overcorrection of their parent functionals.

The most remarkable results of our calculations are the energy splittings obtained with pure DFT calculations (i.e., with spin-independent effective potentials) using the exact exchange functional (third column of Tab.7.1). These spurious splittings are in most cases more than an order of magnitude smaller than the corresponding SDFT results, therefore basically reproducing the exact degeneracy of the different ground-state configurations. Of course, due to the additional variational degree of freedom, total energies in SDFT are always lower than corresponding DFT results. The price to be paid for this improvement, however, are the unphysically increased energy splittings.

| Atom | $\Delta_{jBR}$ [78] | $\Delta_{jPBE}$ [81] | $\Delta^{DFT}_{x-KLI}$ | $\Delta^{SDFT}_{x-KLI}$ | $\Delta^{CSDFT}_{x-KLI}$ |
|---|---|---|---|---|---|
| B | 0.6 | -0.4 | $\approx 0.1$ | 1.7 | 1.4 |
| C | 0.7 | -0.7 | $\approx 0.1$ | 1.6 | 1.3 |
| O | 1.2 | -0.6 | 0.6 | 2.4 | 2.3 |
| F | 1.5 | -0.6 | 0.4 | 2.3 | 2.3 |
| Al | 1.0 | 0.2 | $\approx 0.1$ | 1.7 | 1.6 |
| Si | 0.8 | -0.1 | $\approx 0.1$ | 1.8 | 1.6 |
| S | 2.0 | 0.7 | 0.3 | 3.0 | 3.0 |
| Cl | 1.7 | 0.3 | 0.3 | 3.2 | 3.1 |

Table 6.1: *Spurious energy splittings,* $\Delta = E(|M| = 1) - E(M = 0)$ *in kcal/mol. In all the calculations QZ4P-basis sets has been used.*

### 6.1.3 Results for CSDFT

We now turn to the results of our CSDFT calculations. As expected (see discussion in Sec. 5.2), for zero-current states we always obtain a self-consistent CSDFT solution with vanishing exchange vector potential, $A_x(\mathbf{r}) \equiv 0$. This solution, which is equivalent to the corresponding SDFT solution, always gives the lowest total energy. For current-carrying states we always find a non-vanishing $A_x$. The last column of Tab.7.1 reports the spurious energy splittings between different configurations of open-shell atoms of the first two rows of the periodic table obtained within CSDFT. The splittings are lower in CSDFT than in SDFT due to the additional variational degree of freedom in the former approach. We see that the effect is most pronounced for B and C atoms. Although a CSDFT approach to the degeneracy problem appeared promising, our results show only a small and insufficient improvement.

As discussed in Sec. 5.2, the linear dependence of the KLI equations (5.36) and (5.43) in the asymptotic region may lead to numerical problems in the calculations of the potentials. Problems can also be induced by the use of finite basis sets. For example, while in theory the KS orbitals decay exponentially at a rate determined by their eigenvalues, in a *finite* basis set the orbitals decay at a rate determined by the most diffuse function. We have also obtained exchange vector potentials which diverge asymptotically. This may lead to a wrong ordering of the occupied and unoccupied orbitals or even to convergence problems. A numerically convenient scheme to use the KLI equations (5.36) and (5.43) during the self-consistency cycle consist in, first, to calculate $v_{xc,\sigma}(\mathbf{r})$ from Eq. (5.36) with the $A_{xc}(\mathbf{r})$ obtained in the previous iteration. In this step the asymptotic behavior of $v_{xc,\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} -\frac{1}{r}$ can be imposed if necessary. Then with this updated $v_{xc,\sigma}(\mathbf{r})$, a new $A_{xc}(\mathbf{r})$ is obtained from Eq. (5.43). In order to enforce the asymptotic limit $A_{xc}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} 0$ we add a small positive quantity $\delta$ to $N(\mathbf{r})$ in Eq. (5.49). Total energies and current densities are

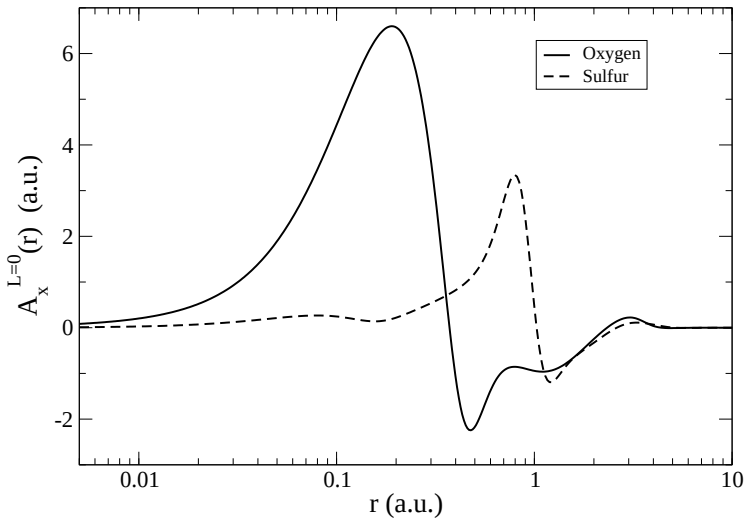


Figure 6.1: *Spherical component of the exchange vector potentials for current-carrying states of oxygen and sulfur atoms (within TZ-basis set).*

very insensitive to the choice of $\delta$: for the fixed value of $\delta = 10^{-4}$ a.u., total energies vary by an order of $10^{-2}$ kcal/mol or less if $\delta$ is varied by an order of magnitude around its chosen value.

In Fig. 6.1 we show the $L = 0$ (i.e., spherical) component of an expansion of the exchange vector potentials in terms of Legendre polynomials, i.e., $A_x(\mathbf{r}) = \sum_{L=0}^{\infty} A_x^L(r) P_L(\cos\theta)$, for the oxygen and sulfur atoms in the current-carrying state. The exchange vector potential of sulfur is smaller in amplitude than the one for oxygen, which also implies a smaller effect on the energies. This confirms our expectations resulting from the analysis of the KLI equations of Sec. 5.2.

### 6.1.4 KLI approximation and finite basis sets

If one looks at the corresponding scalar exchange potential (Fig. 6.2) and magnetic fields (Fig. 6.3), one sees that the overall structure of the SDFT and the CSDFT results are similar. But for $B_x$, there are significant differences in magnitude close to the nucleus.

This is also reflected by a difference in the relative magnetization density $\zeta(0) = [n_\uparrow(0) - n_\downarrow(0)]/[n_\uparrow(0) + n_\downarrow(0)]$ at the nuclear position. For the current-carrying state of oxygen we obtain the value $\zeta(0) = -1.03 \times 10^{-3}$ in SDFT and $\zeta(0) = -1.16 \times 10^{-3}$ in CSDFT which amounts to a difference of approximately 13%. In order to estimate the accuracy of these numerically sensitive results we have also calculated the same quantity for a nitrogen atom and obtain $\zeta(0) = -1.77 \times 10^{-3}$. This value differs by

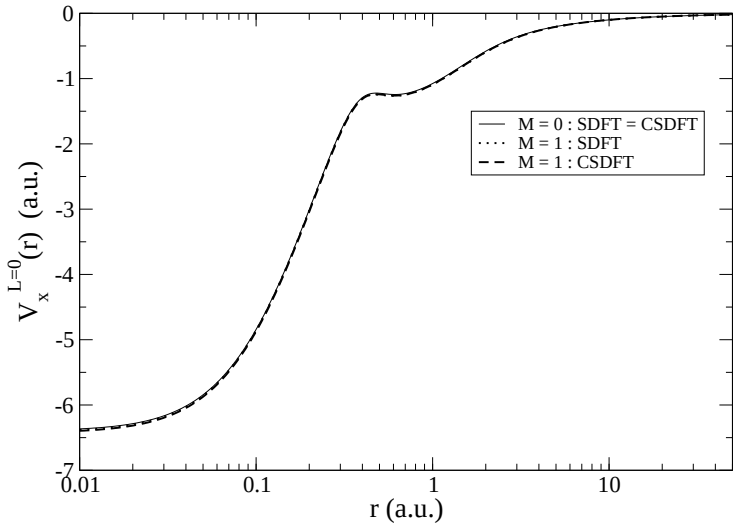


Figure 6.2: *Spherical component of the exchange scalar potentials for the current-carrying state (M=1) and zero current state (M=0) of the oxygen atom computed in SDFT and CSDFT (within TZ-basis set).*

approximately 9% from the value $\zeta(0) = -1.62 \times 10^{-3}$ given in Table 10 of Ref. [38] which was obtained with a fully numerical code for spherically symmetric effective potentials. This analysis refers to results obtained by using the QZ4P basis sets. However, within this basis set, the plots for $v_x$ and $B_x$ show some anomalies. To comment on that, we focus on the SDFT case since the situation for CSDFT is similar.

In Figs. 6.4, starting from around $r = 15$ (a.u.) to around $r = 50$ (a.u.), a small step structure in $v_x$ and a bigger step in $B_x$ are evident. In the region of these steps, the densities are very small and the main contribution comes essentially just from the last occupied orbital (which is decaying exponentially). The contribution to the total energy of this region is only minor. As a result, the overall effect of this numerical artifact is similar to a "constant" shift for the potentials – this is actually quite evident by looking at the up and down potential separately (not reported here), and by the fact that the total energy is not significantly affected. In other words, we observe a kind of "mechanism" through which different potentials computed with a finite basis set can produce if not the same but very close particle densities and hence very close total energies.

We have observed that this kind of anomalies are not present in the results obtained with smaller basis sets, such as TZ - as shown in Figs.6.2 and 6.3 - or with the DZ. The QZ4P basis is the largest set available to us. In particular, it

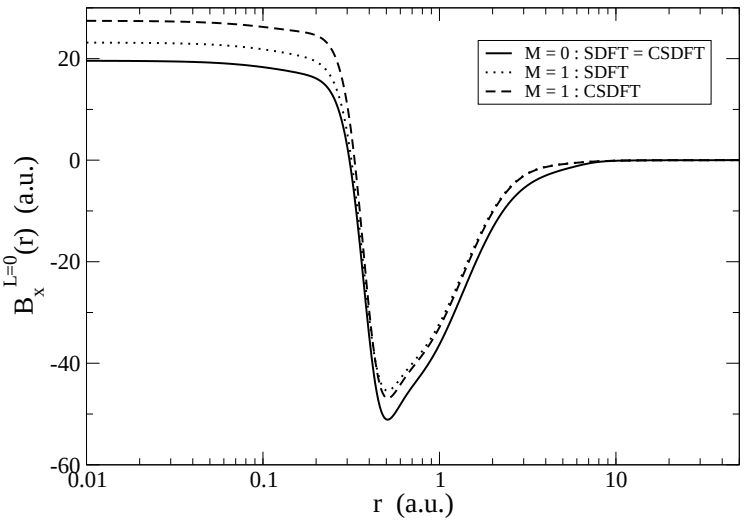


Figure 6.3: *Spherical component of the exchange magnetic field for the current-carrying state (M =1) and zero xurrent state (M=0) of the oxygen atom computed in SDFT and CSDFT (within TZ-basis set).*

has a more diffuse character. Thus, we conclude that to bigger basis sets (but, not yet complete) it may correspond a major flexibility for the potentials to behave wrongly. Always for the QZ4P basis set, we have observed that the problem can be alleviated by adding a small constant to the density appearing in the denominator of Eq. (5.39). In fact, the Slater potential seems to be free from any numerical artifacts (at least for the case considered, and for others that we do not report here). Fig. 6.4 shows the plots before and after this ad-hoc fix, for $\delta = 10^{-4} a.u.$ Remarkably, the difference in the total energy is less than 0.01 kcal/mol. This reminds us of the trick described above, which we used to obtain a non divergent exchange-vector potential. We point out that in recently published work similar problems were reported for the full OEP solution within a finite basis set in (S)DFT [86, 87, 88, 89, 90].

## 6.2 Orbital currents for the correlation energy

In the previous sections, motivated by the observed importance of the exchange-hole curvature and its current-dependent terms, we have studied the performance of the exact-exchange energy functional (which, by definition, describes the curvature correctly) for the energy splittings in DFT, SDFT and CSDFT. In a spin-restricted DFT scheme, the degeneracy is well reproduced to within 0.6 kcal/mol, but surprisingly spin-unrestricted SDFT calculations result in splittings up to 3 kcal/mol

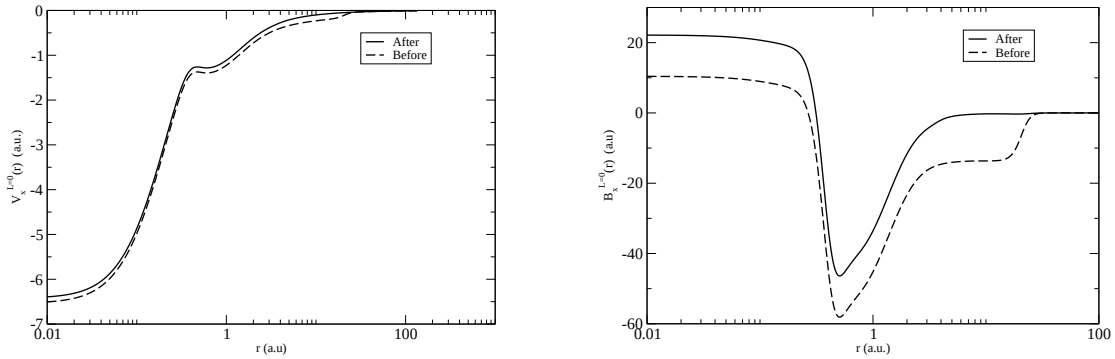


Figure 6.4: *Spherical component of the exchange magnetic field for the current-carrying state of the oxygen atom computed in SDFT; before and after the addition of the constant in the denominator of Eq. (5.39) for the SDFT case.*

work. This is not a very satisfactory result, because SDFT provides solutions of lower energy as DFT, but the corresponding splittings are larger. We also found that current-carrying states always have higher energies than states without current. Moreover, CSDFT results are close to the SDFT ones. These results lead to the conclusion that EXX alone is not sufficient, and inclusion of correlation is needed for any further improvement.

The construction of a correlation energy functional compatible with EXX for the calculation of molecular binding energies is a difficult task [91, 92, 93]. But for spherical atoms, it has been found that EXX combined with the Colle-Salvetti (CS) functional for correlation [94, 95, 96] leads to very accurate results [97]. The CS functional has received a large interest, also because it has been used to derive the popular Lee-Yang-Parr (LYP) functional [98], which is most commonly used together with Becke's exchange functional [99] (BLYP) and in hybrid schemes such as B3LYP [27, 28]. It should be emphasized that the CS correlation energy functional also has its limitations [100, 101, 102]. In particular, while short-range correlations are well described [101] the very important long-range correlations are missing. These correlations often cannot be ignored in molecules and solids, but are energetically negligible in atoms. This fact, together with the encouraging results for spherical atoms [97], indicates that it is appropriate to employ the CS functional to analyze the degeneracy problem for open-shell atoms beyond EXX.

The expression for the CS functional relies on the assumption that the correlated two-body reduced density matrix may be approximated by the Hartree-Fock (HF) two-body reduced density matrix $\rho_2^{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2)$, multiplied by a Jastrow-type correlation factor. After a series of approximations, the following expression is obtained

for the correlation energy

$$E_c = -4c_1 \int d\mathbf{r}\, \frac{\rho_2^{\mathrm{HF}}(\mathbf{r},\mathbf{r})}{\rho(\mathbf{r})} \left\{ \frac{1 + c_2\rho^{-\frac{8}{3}}(\mathbf{r}) \left[ \nabla_s^2 \rho_2^{\mathrm{HF}} \left( \mathbf{r} + \frac{\mathbf{s}}{2}\, , \mathbf{r} - \frac{\mathbf{s}}{2} \right) \Big|_{s=0} \right] e^{-c_3\rho^{-\frac{1}{3}}(\mathbf{r})}}{1 + c_4\rho^{-\frac{1}{3}}(\mathbf{r})} \right\} \tag{6.1}$$

where $\rho_2^{\mathrm{HF}}(\mathbf{r},\mathbf{s})$ is expressed in terms of the average and relative coordinates $\mathbf{r} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ and $\mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2$. Here, $\rho(\mathbf{r})$ is the electron density and the constants $c_1 = 0.049$, $c_2 = 0.132$, $c_3 = 0.2533$, $c_4 = 0.349$ are determined by a fitting procedure using the Hartree-Fock (HF) orbitals for the Helium atom.

Following Lee, Yang and Parr, this expression can be restated as a formula involving only the total charge-density, the charge-density of each Hartree-Fock orbital and their gradient and Laplacian [98]. In this derivation, the single-particle orbitals are tacitly assumed to be real. We denote the resulting expression as CSLYP.

In the following, we relax this restriction and allow for complex orbitals. We then proceed in analogy to the inclusion of current-dependent terms in the Fermi-hole curvature [79, 78] and in the extension of the electron-localization-function (ELF) [103] for time-dependent states [104]. As a consequence, in addition to the term already present in the CSLYP expression, the current densities of the single-particle orbitals appear in the final formula. In order to obtain this expression, which in the following will be denoted as JCSLYP, we rewrite the Laplacian of the Hartree-Fock (HF) two-body reduced density matrix in Eq.(6.1) in terms of the original particle coordinates

$$\nabla_s^2 \rho_2^{\mathrm{HF}} \left( \mathbf{r} + \frac{\mathbf{s}}{2}\, , \mathbf{r} - \frac{\mathbf{s}}{2} \right) \Big|_{s=0} = \left( \frac{1}{4}\nabla_1^2 + \frac{1}{4}\nabla_2^2 - \frac{1}{2}\nabla_1 \cdot \nabla_2 \right) \rho_2^{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2)|_{\mathbf{r}_1=\mathbf{r}_2} \, . \tag{6.2}$$

where

$$\rho_2^{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \frac{1}{2}\sum_\sigma \rho_{1,\sigma}^{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2)\rho_{1,\sigma}^{\mathrm{HF},*}(\mathbf{r}_1,\mathbf{r}_2) \, . \tag{6.3}$$

Here,

$$\rho_{1,\sigma}^{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=1}^{N_\sigma} \varphi_{k,\sigma}(\mathbf{r}_1)\varphi_{k,\sigma}^*(\mathbf{r}_2) \tag{6.4}$$

is the first-order HF density matrix (for a single Slater determinant) expressed in terms of the single-particle orbitals $\varphi_{k,\sigma}(\mathbf{r})$. The corresponding spin-density is simply given by

$$\rho_\sigma(\mathbf{r}) = \rho_{1,\sigma}^{\mathrm{HF}}(\mathbf{r},\mathbf{r}). \tag{6.5}$$

Allowing the single-particle orbitals $\varphi_{k,\sigma}(\mathbf{r})$ to be complex, a given orbital not only gives the contribution $\rho_{k,\sigma}(\mathbf{r}) = |\varphi_{k,\sigma}(\mathbf{r})|^2$ to the density, but also the contribution $\mathbf{j}_{p\ k,\sigma}(\mathbf{r}) = \mathrm{Im}\left(\varphi_{k,\sigma}(\mathbf{r})\nabla\varphi_{k,\sigma}^*(\mathbf{r})\right)$ to the paramagnetic current density which is given by

$$\mathbf{j}_{p,\sigma}(\mathbf{r}) = \sum_{k=1}^{N_\sigma} \mathbf{j}_{p\ k,\sigma}(\mathbf{r}) \, . \tag{6.6}$$

After some straightforward algebra, the Laplacian of the second-order HF reduced density matrix takes the final form

$$\begin{aligned}\nabla_s^2 \rho_2^{\mathrm{HF}} \left( \mathbf{r} + \frac{\mathbf{s}}{2} , \mathbf{r} - \frac{\mathbf{s}}{2} \right) \Big|_{s=0} &= \frac{1}{4} \rho(\mathbf{r}) \nabla^2 \rho(\mathbf{r}) - \frac{1}{4} \left( \nabla \rho(\mathbf{r}) \right)^2 \\ &- \frac{1}{4} \sum_\sigma \rho_\sigma(\mathbf{r}) \nabla^2 \rho_\sigma(\mathbf{r}) + \frac{1}{4} \sum_\sigma \rho_\sigma(\mathbf{r}) \left[ \sum_{k=1}^{N_\sigma} \frac{\left( \nabla \rho_{k,\sigma}(\mathbf{r}) \right)^2}{\rho_{k,\sigma}(\mathbf{r})} \right] \\ &+ J(\mathbf{r}) \end{aligned} \tag{6.7}$$

where

$$J(\mathbf{r}) = \sum_\sigma \rho_\sigma(\mathbf{r}) \left[ -\frac{\mathbf{j}_{p\sigma}^2(\mathbf{r})}{\rho_\sigma(\mathbf{r})} + \sum_{k=1}^{N_\sigma} \frac{\mathbf{j}_{p\ k,\sigma}^2(\mathbf{r})}{\rho_{k,\sigma}(\mathbf{r})} \right] \tag{6.8}$$

contains all the current-dependent terms. Alternatively, Eq. (6.7) may also be expressed in terms of the non-interacting kinetic energy density,

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2} \sum_{k=1}^{N_\sigma} |\nabla \psi_{k,\sigma}(\mathbf{r})|^2 = \frac{1}{8} \sum_{k=1}^{N_\sigma} \frac{\left( \nabla \rho_{k,\sigma}(\mathbf{r}) \right)^2}{\rho_{k,\sigma}(\mathbf{r})} + \frac{1}{2} \sum_{k=1}^{N_\sigma} \frac{\mathbf{j}_{p\ k,\sigma}^2(\mathbf{r})}{\rho_{k,\sigma}(\mathbf{r})} \tag{6.9}$$

as

$$\begin{aligned}\nabla_s^2 \rho_2^{\mathrm{HF}} \left( \mathbf{r} + \frac{\mathbf{s}}{2} , \mathbf{r} - \frac{\mathbf{s}}{2} \right) \Big|_{s=0} &= \frac{1}{4} \rho(\mathbf{r}) \nabla^2 \rho(\mathbf{r}) - \frac{1}{4} \left( \nabla \rho(\mathbf{r}) \right)^2 - \frac{1}{4} \sum_\sigma \rho_\sigma(\mathbf{r}) \nabla^2 \rho_\sigma(\mathbf{r}) \\ &+ \sum_\sigma \left( 2 \rho_\sigma(\mathbf{r}) \tau_\sigma(\mathbf{r}) - \mathbf{j}_{p\sigma}(\mathbf{r})^2 \right) . \end{aligned} \tag{6.10}$$

Comparison of Eqs. (6.7) and (6.10) show that $J(\mathbf{r})$, as defined in Eq. (6.8), also contains current-dependent terms coming from the kinetic energy density.

In the next section, we assess the performance of the CS functional, and, in particular, the relevance of $J(\mathbf{r})$, in reproducing the degeneracy of atomic states.

### 6.2.1 Results for the JCSLYP functional

In analogy to the procedure where Hartree-Fock orbitals are used as input to the CS formula, we have evaluated the correlation energies in a post-hoc fashion using Kohn-Sham orbitals. These orbitals are obtained from a self-consistent EXX-only calculation in the approximation of Krieger, Li, and Iafrate (KLI) [46].

In principle, a given functional should be evaluated with KS orbitals obtained from a self-consistent calculation, and certainly it is possible to use the CS functional in self-consistent calculations [97]. However, we expect only minor quantitative differences between post-hoc evaluation of total energies (or rather total energy differences) and fully self-consistent results because of the variational nature of DFT. In fact, the variational principle implies that if one evaluates the total energy with a

| Atom | SDFT (DFT) | |
|---|---|---|
| | $\Delta_{JCSLYP}$ | $\Delta_{CSLYP}$ |
| B | 0.8 (-0.3) | 2.4 (1.4) |
| C | 0.9 (-0.1) | -3.2 (-4.3) |
| O | -0.6 (-1.9) | 0.9 (-0.4) |
| F | -0.1 (-1.5) | -3.5 (-5.1) |
| Al | 0.4 (-0.5) | 1.1 (0.2) |
| Si | 0.5 (-0.4) | -1.2 (-2.2) |
| S | 0.1 (-1.6) | 1.1 (-0.7) |
| Cl | 0.7 (-1.3) | -1.1 (-3.2) |
| me | 0.3 (-1.0) | -0.4 (-1.8) |
| mae | 0.5 (1.0) | 1.8 (2.2) |

Table 6.2: *Spurious energy splittings,* $\Delta = E(|M| = 1) - E(M = 0)$ *in kcal/mol for open-shell atoms, computed in SDFT (DFT results in parenthesis for comparison). The correlation energy has been added to the KLI-EXX energies including (JCSLYP) and neglecting (CSLYP) the current terms of Eq. (6.7). The last row shows the mean error (me) and mean absolute (mae) of the spurious splittings.*

density which differs slightly from the self-consistent density, the resulting change in the energy is of second order in this small deviation of the densities. This is the reason why in the literature of functional development it is so common that the numerical tests of new approximations are carried out with non-self-consistent calculations. In particular, this is also the reason why in other works on the degeneracy problem the functionals are evaluated in a post-hoc manner as well [77, 78, 81]. We have tested the effect of the self-consistency using a grid-based implementation for spherical atoms: total energies obtained with the Colle-Salvetti functional evaluated with self-consistent and exchange-only KLI densities typically differ by a few tenths of a millihartree which corresponds to a relative deviation of $10^{-3}$ percent.

Table 6.2 shows the spurious energy splittings (difference in the total energies) between Kohn-Sham Slater determinants with total magnetic quantum number $|M| = 1$ and $M = 0$, from our SDFT and DFT calculations. The deviation of these total energies from the exact values is plotted in Fig. 6.5, where again the spurious energy splittings are visible. These results highlight the importance of including $J(\mathbf{r})$ in Eq. (6.7). In particular, it is remarkable to observe that SDFT splittings are within 0.9 kcal/mol (with a mean error of 0.3 kcal/mol and a mean absolute error of 0.5 kcal/mol), and the corresponding DFT spurious energy splittings are less than 1.9 kcal/mol (with mean errors of 1.0 kcal/mol). It is worthwhile to note that in several cases inclusion of correlation leads to current-carrying states ($|M| = 1$) with lower total energy than zero-current states ($M = 0$). These results

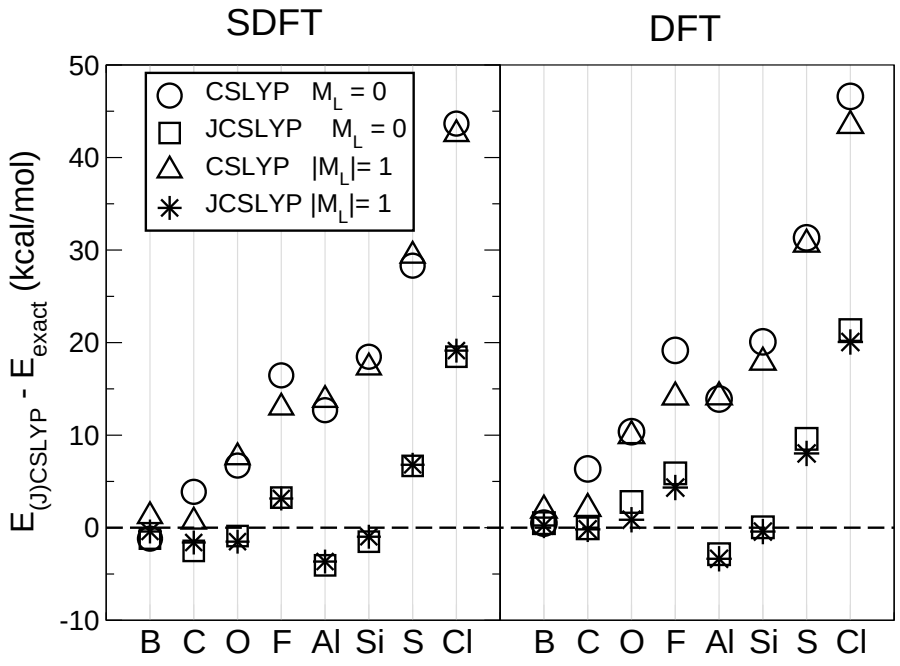


Figure 6.5: *Deviation from exact total energies for SDFT and DFT calculations employing the CS functional, including (JCSLYP) and not including (CSLYP) the current-dependent term J in Eq. (6.7). States with different magnetic quantum numbers $M_L$ are plotted. Exact total energies are taken from Ref. [97] and references therein.*

are in contrast to EXX-only cases, for which we have seen that: (i) the zero-current states are always lowest in energy and (ii) the spurious energy splittings are always smaller in DFT than in SDFT. Therefore, going beyond EXX by including correlation in the form of the CS functional accurate total energies can be obtained within the OEP method [97]. Figure (6.5) and Table (6.3) show the deviations from exact total energies for the states with different magnetic quantum numbers, i.e. different current-carrying states. This further emphasizes the importance of proper inclusion of $J(\mathbf{r})$ in Eq. (6.7).

## 6.3 Conclusions

We confirmed that degenerate ground-state levels of open-shell atoms can be well described by adopting orbital functionals. At the level of EXX (within the KLI approximation) we found that the degeneracy of states with different paramagnetic

| | JCSLYP (CSLYP) | | | |
|---|---|---|---|---|
| | SDFT | DFT | SDFT | DFT |
| $\|M_L\|$ | 0 | 0 | 1 | 1 |
| me | 2.3 (16.1) | 4.7 (18.5) | 2.6 (15.7) | 3.7 (16.8) |
| mae | 4.8 (16.4) | 5.4 (18.5) | 4.7 (15.7) | 4.7 (16.8) |

Table 6.3: *Mean error (me) and mean absolute error (mae) in the total energies for the CS functional, including (JCSLYP) and not including (CSLYP results in parenthesis) the current-dependent term J of Eq. (6.7), in kcal/mol. Exact total energies are taken from Ref. [97] and references therein.*

currents is well reproduced by DFT calculations, but not with SDFT and CSDFT ones. In particular, the additional exchange vector potential of CSDFT does not provide a sufficient correction over the SDFT calculations. Further improvements have been obtained by including the correlation energy. For the Colle and Salvetti correlation functional, we have derived an expression that can be seen as a current-dependent meta-GGA expression. We have evaluated the relevance of the corresponding orbital currents and a very good description of the degeneracy has been obtained.

# Chapter 7

# Extended systems and quantum dots

In the previous chapter, we have seen the role of the exchange vector potential to be only minor in context of the description of the degeneracy of the ground-states of open-shell atoms. It is then interesting to explore if this may be more or less valid also for somewhat different systems. In addition, we are interested in considering situations where the unconstrained treatment of the non-collinear features should be of particularly importance. This leads us to consider extended systems [69, 105]. Finally, we return to finite systems, and the collinear approximation, by considering quantum dots exposed to an external magnetic field [106].

## 7.1 Orbital magnetic moments and band-splittings

CSDFT is the ideal framework to compute quantities such as orbital magnetic moments. In fact, the Kohn-Sham system of CSDFT in addition to the particle density and magnetization density, also reproduces the paramagnetic current of interacting ground-states from which, then, the orbital magnetic moment can be computed as follows

$$\boldsymbol{\mu_L} = \frac{1}{2} \int d^3r \; \mathbf{r} \times \mathbf{j_p}(\mathbf{r}) \; . \tag{7.1}$$

For determining the orbital magnetic moment an approach known as orbital polarization (OP) method [107, 108, 109, 110] is often in use. However, its partial success is plagued by its empirical formulation. Recently, interesting ideas to systematize the OP method within relativistic-density-functional theory (RDFT) [111, 112, 113] have been proposed [114].

In the following, we work within the *non-collinear*, non-relativistic limit, in the form of the Vignale and Rasolt formulation of CSDFT. However, we need to add a relativistic element to the scheme. This is the the spin-orbit coupling. It is well known, in fact, that the inclusion of the spin-orbit coupling is important to avoid the "quenching" of the orbital magnetic moments in crystals. This can be explained

in an intuitive way by considering the fact that the orbital angular momentum does not generate an appropriate symmetry operation for extended systems. The eigenfunction of the crystals must be labeled according to the irreducible representation of the symmetry group of the crystal, which in general have low dimension. Thus the related "orbital moments" are reduced. Moreover, the delocalization of the electrons due to the overlap of the wavefunction with neighboring atoms, leading to a reduction of a kinetic energy as compared to the electron for isolated atoms. However, the spin magnetic moments are not quenched and thus the spin-orbit coupling can act to enhance the orbital magnetic moments. The quenching of the orbital moments in absence of the spin-orbit coupling term has been observed also in CSDFT calculations using the local vorticity approximation [115]. We anticipate here, that we have experienced the same effect by using the EXX approximation. An additional reason for considering the spin-orbit coupling is to reproduce the observed degeneracy splitting in the electronic band-structures.

### 7.1.1 Numerical implementation

A suitable functional to be used in the corresponding non-collinear OEP method, is the exact-exchange-orbital functional evaluated with KS spinors

$$E_{\mathrm{x}}^{\mathrm{EXX}}[\{\Phi_i\}] \equiv -\frac{1}{2}\int\int d^3r\, d^3r' \sum_{i,j}^{\mathrm{occ}} \frac{\Phi_i^\dagger(\mathbf{r})\Phi_j(\mathbf{r})\Phi_j^\dagger(\mathbf{r}')\Phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,. \tag{7.2}$$

For the calculations we have implemented the scheme for the solution of the *non-collinear* OEP equations in CSDFT - described in Sec. 5.1.1 - using the FP-LAPW method [116] within the EXCITING code [117]. The single-electron problem is solved using an augmented plane wave basis without using any shape approximation for the effective potential. Likewise, the magnetization and current densities and their conjugate fields are all treated as unconstrained vector fields throughout space. The deep lying core states (3 Ha below the Fermi level) are treated as Dirac spinors and valence states as Pauli spinors. To obtain the Pauli spinor states, the Hamiltonian containing only the scalar fields is diagonalized in the LAPW basis: this is the first-variational step. The scalar states thus obtained are then used as a basis to set up a second-variational Hamiltonian with spinor degrees of freedom, which consists of the first-variational eigenvalues along the diagonal, and the matrix elements obtained from the external and effective vector fields. This is more efficient than simply using spinor LAPW functions, but care must be taken to ensure that there is a sufficient number of first-variational eigenstates for convergence of the second-variational problem. Spin-orbit coupling is also included at this stage [115, 118, 119, 120].

| | | SDFT | | | CSDFT |
|---|---|---|---|---|---|
| Solid | Exp. | LSDA | GGA | EXX | EXX |
| Fe | 0.08 | 0.053 | 0.051 | 0.034 | 0.034 |
| Co | 0.14 | 0.069 | 0.073 | 0.013 | 0.013 |
| Ni | 0.05 | 0.038 | 0.037 | 0.029 | 0.029 |
| | | 36.2 | 36.7 | 63.4 | 63.4 |

Table 7.1: *Orbital magnetic moments for iron, cobalt and nickel in $\mu_B$. The experimental data are taken from Ref. [121]. All calculations are performed in the presence of spin-orbit coupling. The final row lists the average percentage deviation from the experimental value.*

| Symmetry | | SDFT | | | | |
|---|---|---|---|---|---|---|
| point | Exp. | LSDA | GGA | EXX | EXX-CSDFT | EXX-SCDFT |
| Ge $\Gamma_{7v-8v}$ | 297 | 311 | 296 | 291.3 | 289 | 258.1 |
| Ge $\Gamma_{6c-8c}$ | 200 | 229.7 | 220 | 201.3 | 199 | 173.3 |
| Si $\Gamma_{25v}$ | 44 | 50 | 58 | 42.5 | 45.5 | 42.5 |
| | | 9.5 | 14.0 | 2.0 | 2.2 | 10.5 |

Table 7.2: *Spin-orbit induced splittings for Germanium and Silicon at the $\Gamma$-point, in meV. The symmetry point at which the results are obtained is indicated in column one. The experimental data are taken from Ref. [122]. EXX-CSDFT are results of the present work and EXX-SCDFT are results from Ref. [123]. The final row lists the average percentage deviation from the experimental value.*

### 7.1.2 Results and discussion

The orbital moments for spontaneous magnets Fe, Co and Ni, in the absence of external magnetic fields and with spin-orbit coupling included, are presented in Table 7.1.

For SDFT, the LSDA, GGA and EXX functionals are used, while for CSDFT the values are obtained using the EXX functional. It is clear from Table 7.1 that there is *no difference* between the results obtained using EXX-CSDFT and EXX-SDFT. It should also be noted that in comparison to experiments the EXX results are significantly worse than their LSDA and GGA counterparts. One reason, of course, could be the fact that LSDA and GGA also include correlation in an approximate way which is neglected completely within the EXX framework.

The spin-orbit coupling is also responsible for the splitting of some degeneracy of the band structure. In a recent work [123] it is claimed that the use of the EXX functional in the framework of spin-current-DFT (SCDFT) [52, 124, 125] improves the spin-orbit induced splitting of the bands in semiconductors. Unfortunately, it is not clear if this improvement is due to the use of different functionals (going

from LSDA to EXX), or due to the use of an extra density when going from SDFT to CSDFT. This has motivated us to compare CSDFT and SDFT results for this quantity using the same functional in both cases. We have determined the value of this splitting for solid Si and Ge and the results are presented in Table 7.2. While the EXX functional significantly improves the agreement with experimental values, there is almost no change when going from SDFT to CSDFT. Thus the improvement is solely due to the orbital-based functional. We also note that the EXX-SCDFT results of Ref. [123] are significantly different from ours, and in much worse agreement with experiments. This might be due to the use of pseudopotentials in the previous work. In this respect it is worth noting that EXX derived KS energy gaps also show significant differences depending on whether an all-electron full-potential or pseudopotential method is used [126].

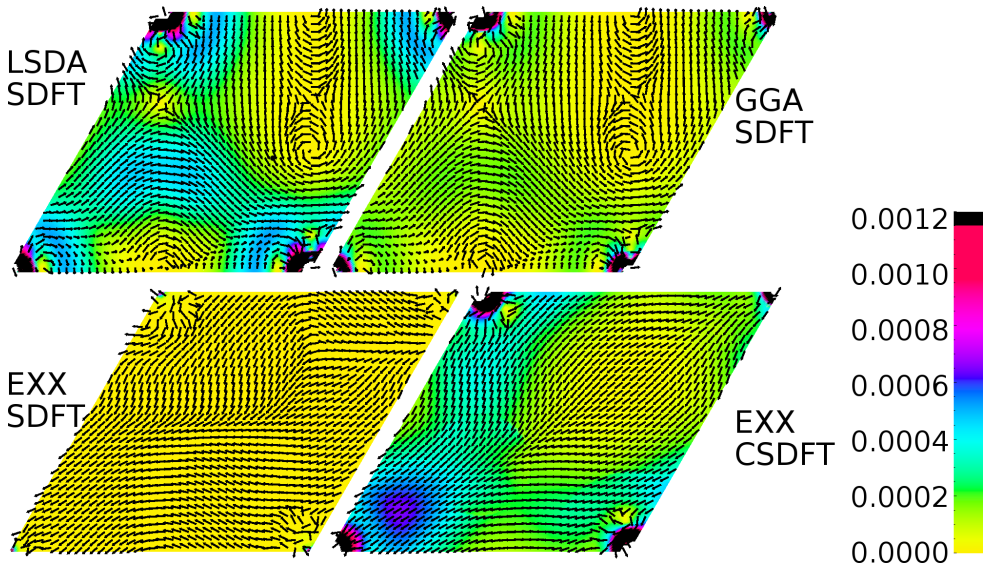


Figure 7.1: *Paramagnetic current density for Ge, in the [110] plane, calculated using the SDFT and CSDFT. Arrows indicate the direction and information about the magnitude (in atomic units) is given in the colour bar.*

The paramagnetic current density of Ge for LSDA, GGA, EXX-SDFT and EXX-CSDFT is plotted in Fig. 7.1 . Ge is chosen as an example since the spin-orbit induced splitting is largest for this system and, unlike in the case of metallic orbital moments, this quantity does show some difference when going from SDFT to CSDFT. We immediately notice that there is no significant qualitative difference between the LSDA and GGA currents. There are, however, pronounced differences in the current density between LSDA/GGA and EXX-(C)SDFT: the current in the

latter case being smaller and more homogeneous than that of the former. This is an interesting finding since it indicates the tendency of (semi-) local functionals towards higher values of the paramagnetic current density. Even though the EXX-SDFT current is considerably lower in magnitude than that of EXX-CSDFT and also has a less symmetric structure, the spin-orbit splittings for the two cases are almost the same. From Fig. 1 it is also clear that one of the major effects of using the OEP method and of using $\mathbf{j}_p$ as an extra density is to change the local structure of the paramagnetic current.

While the spin-orbit induced band splittings in exact-exchange calculations (both SDFT and CSDFT ones) are in rather good agreement with experiment, the results for the orbital moments are worse than the LSDA or GGA values. This suggests that the proper treatment of correlation is essential for the accurate calculation of orbital moments.

## 7.2 Non-collinearity in SDFT

Let us remind that, electron-gas-based approximations have been developed from the collinear ground-state of the electron-gas. As a consequence, they can be applied only under the assumption of either local or global collinearity of the magnetization density and the exchange-correlation magnetic field. In the former case, the practical scheme of calculation is as follows: one defines for each point in space a rotation wich diagonalizes the spin-density matrix [64, 71]. In such a way, a magnetization along the local $z$-direction is obtained from which a corresponding (parallel) exchage-correlation magnetic field can be computed. Then, the fields are rotated back. Hence, the resulting magnetization density and exchange-correlation magnetic field are by construction locally collinear.

Instead, exchange-correlation functionals of Kohn-Sham spinors naturally allow an *unconstrained* non-collinear calculation. As an example in Fig. 7.2, we report the plot of $\mathbf{m}(\mathbf{r}) \times \mathbf{B}_{\mathrm{EXX}}(\mathbf{r})$ for the case of an unsupported Cr monolayer, for which non collinearity is thus apparent. Although for this particular case, one might speculate that inclusion of correlation may reduce the non-collinearity of $\mathbf{m}(\mathbf{r})$ and the resulting $\mathbf{B}_{\mathrm{xc}}(\mathbf{r})$, in general such non-collinear features are expected to exist.

Although the property of local non-collinearity between the magnetization and the exchange-correlation magnetic field so far only has been demonstrated for static systems, it is of particular interest for time-dependent SDFT with respect to applications for spin dynamics. The Kohn-Sham equation for time-dependent SDFT [37] is given by

$$i\frac{\partial}{\partial t}\Phi_k(\mathbf{r},t) = \left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r},t) + \mu_B \boldsymbol{\sigma}\mathbf{B}_s(\mathbf{r},t)\right)\Phi_k(\mathbf{r},t)\ . \tag{7.3}$$

Using this equation, it can be shown [127] that the time evolution of the mag-

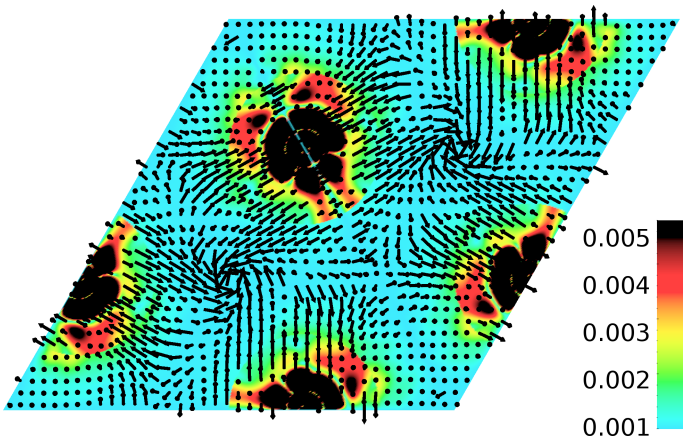


Figure 7.2: $\mathbf{m}(\mathbf{r}) \times \mathbf{B}_{\mathrm{EXX}}(\mathbf{r})$ *for an unsupported Cr monolayer. Arrows indicate the direction and information about the magnitude (in a.u.) is given in the color bar.*

netization density is governed by the equation

$$\frac{\partial \mathbf{m}(\mathbf{r},t)}{\partial t} + \nabla \mathbf{J}_{KS}(\mathbf{r},t) = -2\mu_B\, \mathbf{m}(\mathbf{r},t) \times \mathbf{B}_s(\mathbf{r},t)\ , \tag{7.4}$$

where the Kohn-Sham spin-current tensor is given by

$$\Big[\mathbf{J}_{KS}(\mathbf{r},t)\Big]_{\alpha\beta} = \frac{\mu_B}{2i} \sum_{k=1}^{N} \left\{ \left[\frac{\partial}{\partial r_\beta} \Phi_k^\dagger(\mathbf{r},t)\right] \sigma_\alpha \Phi_k(\mathbf{r},t) - \Phi_k^\dagger(\mathbf{r},t) \sigma_\alpha \left[\frac{\partial}{\partial r_\beta} \Phi_k(\mathbf{r},t)\right] \right\} \tag{7.5}$$

and the divergence of this tensor is defined as

$$\Big[\nabla \mathbf{J}_{KS}(\mathbf{r},t)\Big]_{\alpha} := \sum_{\beta=1}^{3} \frac{\partial}{\partial r_\beta} \Big[\mathbf{J}_{KS}(\mathbf{r},t)\Big]_{\alpha\beta}\ . \tag{7.6}$$

The right-hand side of Eq. (7.4) contains a term proportional to $\mathbf{m}(\mathbf{r},t) \times \mathbf{B}_{xc}(\mathbf{r},t)$, which in LSDA vanishes identically. Hence, only with spinor-orbital functionals such as EXX, a reasonable description of the spin dynamics can be achieved.

## 7.3 Quantum dots in an external magnetic field

Quantum dots represent a fundamental element for novel nanoelectronic components based on the semiconductor technology, and a paradigm for exploring a large spectrum of quantum effects in finite low-dimensional systems [128, 129]. A common way to fabricate quantum dots is to restrict the two-dimensional electron gas in a semiconductor heterostructure laterally by electrostatic gates, or vertically by etching techniques: this creates a bowl-like potential in which conduction electrons

are trapped. Their realization can be easily tuned by changing the electrostatic gates, their geometry, or applying magnetic fields. The electrons in a quantum dot are affected by the surrounding semiconductor material. One can describe electron motion in a quantum dot by replacing the mass of a free electron by the effective mass of electrons of the host semiconductor material in the Hamiltonian ($m \to m^*$). This is called the effective-mass approximation and it has been shown to be fairly accurate for the quantum dots we are going to consider.

In modelling quantum dots, the most common approximation for the flat disk-like shape is a two-dimensional well with a parabolic confinement potential. Due to the cylindrical symmetry of the problem, the model quantum dot Hamiltonian of $N$ electrons in a homogeneous external magnetic field along the $z$-axis can be separated into radial and angular parts as $\varphi_{jl\sigma}(\mathbf{r}) \sim \exp(il\theta)R_{jl\sigma}(r)$, where the radial wave functions $R_{jl\sigma}(r)$ are eigenfunctions of the Hamiltonian

$$\hat{H}_{sl\sigma} = -\frac{1}{2m^*}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{l^2}{r^2}\right) + \frac{l}{2}\omega_c + m^*\frac{\Omega^2}{2}r^2 + \frac{l}{m^*c}\frac{A_{xc}(r)}{r} \pm \mu_B m^* g^* B_0 + v_H(r) + v_{xc\sigma}(r) \tag{7.7}$$

with the total confinement $\Omega = \sqrt{\omega_0^2 + \omega_c^2/4}$, and the cyclotron frequency $\omega_c = B_0/m^*c$. The radial wave functions are expanded in the basis of eigenfunctions of the corresponding non-interacting problem. Before reporting our results, it is appropriate to mention that although the Hamiltonian of SDFT does not include any coupling to the external vector potential, in practice this coupling is usually included. As a result, the Kohn-Sham schemes of SDFT and CSDFT use the same external vector potential, but the latter also includes the exchange-correlation vector potential.

Figure 7.3 shows the total energy of a six-electron-quantum dot ($\omega_0 = 5$ meV) as a function of the strength of the external magnetic field $B_0$. The kinks correspond to changes in the ground-state configurations with respect the $z$-projection of the angular momenta $(L_z; S_z)$. The EXX total energies are considerably too large when compared with the accurate QMC results [54]. EXX also leads to an erroneous occurrence of the $(-5; 2)$ ground-state at $B_0 = 1.5...2.0$ T. Moreover, we find only negligible effects of $A_x$ on physical quantities like the total energy, density, and current density. In this respect, our results are in line with previous ones obtained within several kinds of local approximations [54].

Interestingly, adding the LSDA correlation [130] in a post-hoc fashion to the EXX energies ($EXX + cLSDA$) yields the correct sequence of states as a function of $B_0$. This is a major improvement over the cLSDA-corrected Hartree-Fock calculation which does not give the correct ground states for a similar system [131]. As seen in Fig. 7.3, the energies of EXX+cLSDA are still consistently too low by $1.0-1.5$ meV. Considering the agreement between QMC and the *conventional* LSDA, our results reflect the inherent tendency of the LSDA to cancel out its respective errors in exchange and correlation. We are able to remove most of the error by applying

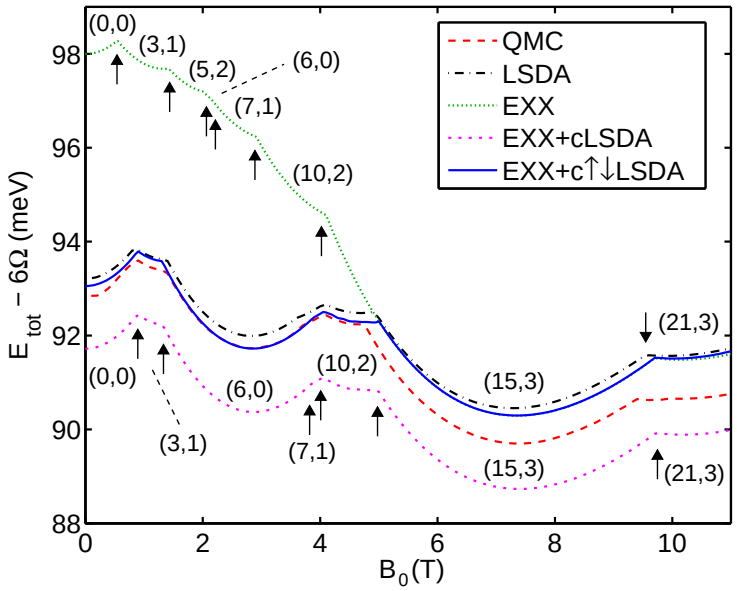


Figure 7.3: *Magnetic-field dependence of the total ground-state energy (minus* $6\Omega = 6\sqrt{\omega_0^2 + \omega_c^2/4}$*) in the six-electron quantum dot calculated with the exact-exchange (EXX), EXX plus LSDA correlation (EXX+cLSDA), and with EXX plus the corrected LSDA correlation (EXX+c↑↓LSDA). The LSDA and quantum Monte Carlo (QMC) results [54] are shown for comparison.*

a self-interaction correction as suggested by Stoll et al. [132], which consists in removing the contribution coming from the like-spin electrons, as follows

$$E_{c,\uparrow\downarrow} = E_{c,LSDA} - \int d\mathbf{r} n_\uparrow(\mathbf{r}) \varepsilon_c[n_\uparrow, 0](\mathbf{r}) - \int d\mathbf{r} n_\downarrow(\mathbf{r}) \varepsilon_c[0, n_\downarrow](\mathbf{r}), \qquad (7.8)$$

where $\varepsilon_c(n_\uparrow, n_\downarrow)$ is the correlation energy per electron of the two-dimensional polarized-electron-gas of Attaccalite et al. [130]. In Fig. 7.3, we have denoted this approximation as EXX+c↑↓LSDA.

Finally – as we have mentioned in Sec. 6.2.1 – we would like to emphasize once more that our post-hoc calculations are justified by the variational nature of DFT. This implies that if one evaluates the total energy with a density which slightly differs from the self-consistent density, the resulting change in the energy is of second order in this small deviation of the densities.

## 7.4 Conclusions

We have verified that for extended system such as Fe, Co, Ni, Ge and Si and for quantum dots in external magnetic fields, the effect of full self-consistent EXX cal-

culations within CSDFT is only minor, and often negligible, as compared to self-consistent EXX-SDFT calculations. In particular, the orbital magnetic moments for Fe, Co, Ni are greatly underestimated both in EXX-SDFT and EXX-CSDFT. The possibility of carrying out ab-initio non-collinear calculation within our extended formalism has been highlighted by reporting the case of an unsupported Cr monolayer. For the case of quantum dots exposed to external magnetic fields, it is seen that a modified SDFT scheme including the coupling to the vector potential, but not adding the dependence of the functional on the currents, can provide energies close to the quantum Monte Carlo total energies, if a self-interaction corrected LSDA for correlation is added to the EXX functional.

# Chapter 8

# Exchange-energy functionals for 2D systems

Since the advent of density-functional theory (DFT) much effort went in the development of approximative functionals for the exchange and correlation energies. Most of this work focused on three-dimensional (3D) systems. For two-dimensional (2D) systems such efforts have been relatively scarce, partly due to the lack of direct applications until significant developments in semiconductor technology allowed the fabrication of low-dimensional structures such as quantum dots (QDs). Semiconductor QDs are finite quasi 2D electron systems confined typically in GaAs/AlGaAs heterostructures, and due to their controllability in size, shape, and number of confined electrons, they have various applications in the field of nanotechnology [128, 129]. Within the DFT approach, QDs are most commonly treated using the 2D LSDA exchange functional derived in 1977 by Rajagopal and Kimball [133], which is then combined with the 2D LSDA correlation parametrized first by Tanatar and Ceperley [134] and later for the complete range of collinear spin polarization by Attaccalite and co-workers [130]. Despite the relatively good performance of LSDA with respect to, e.g., quantum Monte Carlo calculations [54], there is a lack of accurate 2D functionals. Moreover, previous studies have shown that 3D functionals perform poorly when applied to these quasi 2D systems [135, 136, 137]. For example, in 3D the LDA-exchange is proportional to $n^{4/3}$ whereas in 2D is proportional to $n^{3/2}$. In fact, Pollack and Perdew [137] analyzed very nicely that when a density becomes more and more 2D, the 3D LDA results become increasingly worse. This failure is common to GGA and meta-GGA approximations as well. The exact-exchange functional employed within the optimized effective potential method, which automatically conforms to various dimensionalities, seems an appealing alternative. However, the development of approximations for the correlation energies compatible with exact exchange remains a challenging problem. In this chapter, we present an ab initio derivation of new exchange functionals for finite 2D systems [138] in the framework proposed by Becke and Roussel [80]. The new exchange-energy functionals constitute a natural basis for developing corresponding correlation-energy

functionals.

## 8.1 Modeling the exchange-hole function

Our starting point is the expression of the exchange energy given in terms of the spin-dependent exchange-hole functions, which reads as

$$E_x[n_\uparrow, n_\downarrow] = -\frac{1}{2}\sum_\sigma \int d^2r_1 \int d^2r_2 \; \frac{n_\sigma(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} h_x^\sigma(\mathbf{r}_1, \mathbf{r}_2) \; . \tag{8.1}$$

Within the restriction that the noninteracting ground state is nondegenerate and hence takes the form of a single Slater determinant, the exchange-hole (or Fermi-hole) function $h_x^\sigma$ takes the form

$$h_x^\sigma(\mathbf{r}_1, \mathbf{r}_2) = \frac{|\sum_{k=1}^{N_\sigma} \psi_{k,\sigma}^*(\mathbf{r}_1)\psi_{k,\sigma}(\mathbf{r}_2)|^2}{n_\sigma(\mathbf{r}_1)}. \tag{8.2}$$

The sum in the numerator is the one-body spin-density matrix of the Slater determinant in terms of the KS orbitals, $\psi_{k,\sigma}$. The exchange-hole function as defined here is always positive. Moreover, integrating this function over $\mathbf{r}_2$ yields

$$\int d^2r_2 \; h_x^\sigma(\mathbf{r}_1, \mathbf{r}_2) = 1. \tag{8.3}$$

This property reflects that around an electron with spin $\sigma$ at $\mathbf{r}_1$ other electrons of the same spin are less likely to be found as a consequence of the Pauli principle. From Eq. (8.1), specializing it to the case of 2D, it is clear that to evaluate the exchange energy we just need to know the cylindrical average with respect to $\mathbf{s} = \mathbf{r_2} - \mathbf{r_1}$ of the exchange-hole around $\mathbf{r}_1$. Expressing the exchange-hole by its Taylor expansion

$$h_x^\sigma(\mathbf{r}_1, \mathbf{r}_2 = \mathbf{r}_1 + \mathbf{s}) = \exp(\mathbf{s}\cdot\nabla')h_x^\sigma(\mathbf{r}_1, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_1}, \tag{8.4}$$

the *cylindrical* average is defined as

$$\bar{h}_x^\sigma(\mathbf{r}_1, s) = \frac{1}{2\pi}\int_0^{2\pi} d\phi_s \exp(\mathbf{s}\cdot\nabla')h_x^\sigma(\mathbf{r}_1, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_1}. \tag{8.5}$$

The short-range behavior with respect to $s$ is then obtained as

$$\begin{aligned} \bar{h}_x^\sigma(\mathbf{r}_1, s) &= n_\sigma(\mathbf{r}_1) + \frac{s^2}{4}\nabla'^2 h_x^\sigma(\mathbf{r}_1, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_1} + ... \\ &= n_\sigma(\mathbf{r}_1) + s^2 C_{x,\sigma}(\mathbf{r}_1) + ... \end{aligned} \tag{8.6}$$

where $C_x^\sigma$ is the so-called local curvature of the exchange hole around the given reference point $\mathbf{r}_1$. This function can be expressed as [80, 79]

$$C_x^\sigma = \frac{1}{4}\left[\nabla^2 n_\sigma - 2\tau_\sigma + \frac{1}{2}\frac{(\nabla n_\sigma)^2}{n_\sigma} + 2\frac{\mathbf{j}_{p,\sigma}^2}{n_\sigma}\right], \tag{8.7}$$

where

$$\tau_\sigma = \sum_{k=1}^{N_\sigma} |\nabla\psi_{k,\sigma}|^2 \tag{8.8}$$

is *twice* the spin-dependent kinetic-energy density, and

$$\mathbf{j}_{p,\sigma} = \frac{1}{2i}\sum_{k=1}^{N_\sigma}\left[\psi^*_{k,\sigma}\left(\nabla\psi_{k,\sigma}\right) - \left(\nabla\psi^*_{k,\sigma}\right)\psi_{k,\sigma}\right] \tag{8.9}$$

is the spin-dependent paramagnetic current density. Both $\tau_\sigma$ and $\mathbf{j}_{p,\sigma}$ depend explicitly on the KS orbitals. Thus the expression in Eq. (8.7) has an implicit dependence on the spin-densities $n_\sigma$. Once we can provide an approximation for $\bar{h}^\sigma_x(\mathbf{r}_1, s)$ satisfying the normalization condition of Eq. (8.3), we can compute the exchange-hole potential

$$U^\sigma_x(\mathbf{r}_1) = -2\pi\int_0^\infty ds\ \bar{h}^\sigma_x(\mathbf{r}_1, s) \tag{8.10}$$

and finally the exchange energy

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}\sum_\sigma \int d^2r_1\ n_\sigma(\mathbf{r}_1)U^\sigma_x(\mathbf{r}_1). \tag{8.11}$$

As the basis of our exchange model we consider the ground state single-electron wave function of a 2D harmonic oscillator

$$\psi_\sigma(\mathbf{r}) = \frac{\alpha}{\sqrt{\pi}}\exp\left[-\frac{\alpha^2 r^2}{2}\right], \tag{8.12}$$

which is normalized for each $\alpha \neq 0$. We point out that the harmonic (parabolic) approximation for the confinement potential is the most common choice when modeling QDs fabricated in semiconductor heterostructures [128, 129]. The exact exchange-hole function (8.2) for the single-particle case becomes $h^\sigma_x(\mathbf{r}_1, \mathbf{r}_2) = \psi^*_\sigma(\mathbf{r}_2)\psi_\sigma(\mathbf{r}_2) = n_\sigma(\mathbf{r}_2)$. Setting $\mathbf{r}_1 = \mathbf{r}$ and $\mathbf{r}_2 = \mathbf{r} + \mathbf{s}$, we calculate the cylindrical average as

$$\begin{aligned}
\bar{h}^\sigma_x(\mathbf{r}, s) &= \frac{1}{2\pi}\int_0^{2\pi} d\phi_s n_\sigma(\mathbf{r}+\mathbf{s}) \\
&= \frac{\alpha^2}{2\pi^2}\exp\left[-\alpha^2\left(r^2+s^2\right)\right]\times \\
&\times \int_0^{2\pi} d\phi_s \exp\left[-2\alpha^2 rs\cos(\phi)\right] \\
&= \frac{\alpha^2}{\pi}\exp\left[-\alpha^2\left(r^2+s^2\right)\right] I_0(2\alpha^2 rs),
\end{aligned} \tag{8.13}$$

where $I_0(x)$ is the modified Bessel function of the first kind of zero order (note that $I_0(0) = 1$). Performing the integral in Eq. (8.10) yields

$$U^\sigma_x(r) = -|\alpha|\sqrt{\pi}\exp\left[-\alpha^2 r^2/2\right] I_0(\alpha^2 r^2/2) \tag{8.14}$$

for the exchange-hole potential. Since the modified Bessel function has the limiting property $I_0(x) \to \exp(x)/\sqrt{2\pi x}$, for $x \to +\infty$ ($x \in \mathbb{R}$), we immediately find

$$\lim_{r\to\infty} U_x^\sigma(r) = -1/r. \tag{8.15}$$

Furthermore, this particular case is self-interaction free by construction.

### 8.1.1 Implicit density functional

At this point, we adopt the strategy of Becke and Russel [80] and elevate expression (8.13) as a general model for the averaged exchange hole of a generic $N$-electron 2D system. In order to locally reproduce the short-range behavior of the exchange hole, we replace $\alpha^2$ and $r^2$ by functions of $r$, respectively, i.e., $\alpha^2 \to a(r)$ and $r^2 \to b(r)$. Now we can rewrite Eq. (8.13) as

$$\bar{h}_x^\sigma(a, b; s) = \frac{a}{\pi} \exp\left[-a\left(b + s^2\right)\right] I_0(2a\sqrt{b}s). \tag{8.16}$$

This model satisfies, through its original definitions, $\bar{h}_x^\sigma(a, b; s) \geq 0$ and the unit normalization [Eq. (8.3)]. From the second-order term in the Taylor expansion in Eq. (8.6) we obtain

$$(y - 1)\exp(y) = \frac{1}{\pi}\frac{C_x^\sigma}{n_\sigma^2}, \tag{8.17}$$

where $y := ab$. The first-order term gives

$$a = \pi n_\sigma \exp(y), \tag{8.18}$$

and hence we get

$$b = \frac{y}{\pi n_\sigma} \exp(-y). \tag{8.19}$$

As the result, Eqs. (8.17)-(8.19) determine, together with Eqs. (8.16), (8.10) and (8.11), an implicit density functional. This completes the derivation of our first approximation to the exchange-energy functional.

### 8.1.2 Explicit density functional

Next we show that the same procedure also provides an explicit density functional. For that purpose, we consider the 2DEG limit where the derivatives in Eq. (8.7) can be set to zero, i.e., $\nabla^2 n_\sigma = 0$ and $\nabla n_\sigma = 0$, and we take the known expression for the kinetic-energy density of the 2DEG, $\tau_\sigma = 2\pi\rho_\sigma^2 + \frac{\mathbf{j}_{p,\sigma}^2}{\rho_\sigma}$ (Ref. [139]). Note that the current-dependent term in Eq. (8.7) cancels the current-contribution to the kinetic energy, leading to the expected result that the exchange energy of a uniform system does not depend on the (uniform) paramagnetic current density. In fact, a uniform paramagnetic-current in a homogeneous electron gas can be viewed as being

generated by a transformation to a moving Galilei frame. Since the electron-electron Coulomb interaction is the same in any Galilean frame, the exchange energy cannot depend on the Galilean frame and, hence, must be independent of the uniform paramagnetic-current density. These simplifications lead to $y = 0$, $b = 0$, and $a = \pi n_\sigma$, so that the averaged exchange-hole function becomes

$$\bar{h}_x^\sigma(s) = n_\sigma \exp\left[-\pi n_\sigma s^2\right], \tag{8.20}$$

and the exchange-hole potential is now given by $U_x^\sigma[n_\sigma] = -\pi n_\sigma^{1/2}$, which is an explicit functional of the spin-density. Defining the 2D density parameter $r_s = 1/\sqrt{\pi n}$, where $n = n_\uparrow + n_\downarrow$ is the total density, and the polarization $\xi = (n_\uparrow - n_\downarrow)/n$, the total exchange energy per particle becomes

$$\epsilon_x[r_s, \xi] = -\frac{\sqrt{\pi}}{4\sqrt{2}\, r_s}\left[(1+\xi)^{3/2} + (1-\xi)^{3/2}\right]. \tag{8.21}$$

This expression can then be used also for inhomogeneous systems of electrons by assuming that locally they behave as homogenoues one. In fact, it is interesting to compare expression (8.21) with the exact 2DEG result [133] widely applied to finite systems in terms of the LSDA:

$$\epsilon_x^{\mathrm{2DEG}}[r_s, \xi] = -\frac{2\sqrt{2}}{3\pi r_s}\left[(1+\xi)^{3/2} + (1-\xi)^{3/2}\right]. \tag{8.22}$$

Interestingly, the only difference between these two expressions is in the prefactor for about $\sim 4.4\%$.

## 8.2 Evaluation of the new functionals

In this section we report the numerical evaluation of the performance of our new approximations considering as reference systems the two-dimensional electron gas and few electrons quantum dots.

### 8.2.1 Two-dimensional electron gas

Besides the exchange energies, it is interesting to compare the averaged exchange hole given in Eq. (8.20) with the exact exchange hole of the 2DEG. Following the derivation of Gori-Giorgi and co-workers [140] for the pair-distribution function of the 2DEG, we find

$$\bar{h}_{x,\sigma}^{\mathrm{2DEG}}(s) = \frac{\left(k_{F,\sigma}^{\mathrm{2D}}\right)^2}{\pi}\frac{J_1^2(k_{F,\sigma}^{\mathrm{2D}} s)}{(k_{F,\sigma}^{\mathrm{2D}} s)^2}, \tag{8.23}$$

where $k_{F,\sigma}^{\mathrm{2D}} = (4\pi n_\sigma)^{1/2}$ is the Fermi momentum (for spin $\sigma$) in 2D, and $J_1$ is the ordinary Bessel function of the first order. In Fig. 8.1(a) we compare the exchange holes

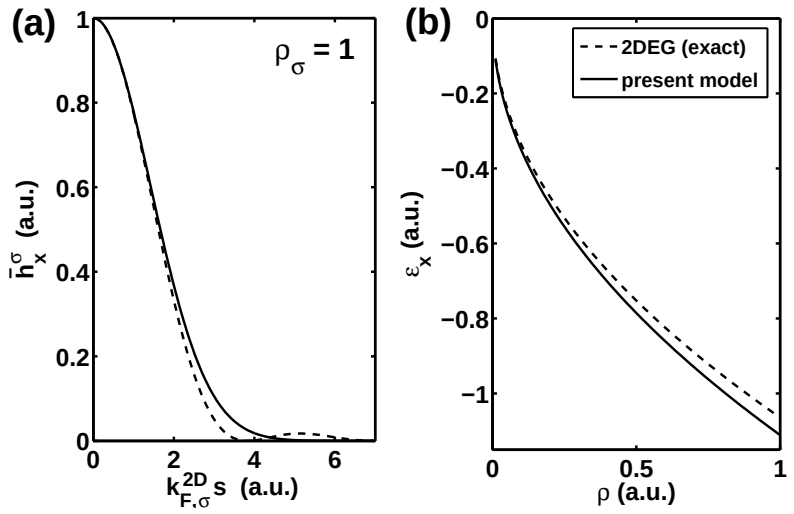


Figure 8.1: *Exchange hole (a) and the exchange energy per particle (b) for two-dimensional electron gas ($\xi = 0$) in the exact expression (dashed lines) and in the present model (solid lines).*

with a fixed spin-density $n_\sigma = 1$ between our model (solid lines) and the exact 2DEG result (dashed lines) and find a good qualitative agreement. Figure 8.1(b) demonstrates the differences in the exchange energies (per particle) given in Eqs. (8.21) and (8.22) as a function of the total density (for $\xi = 0$).

### 8.2.2 Few-electron quantum dots

Next, we consider the smallest nontrivial QD consisting of two electrons. The Hamiltonian is given by

$$H = \sum_{i=1}^{2} \left( -\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega_0^2 r_i^2 \right) + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}, \tag{8.24}$$

where we set the strength of the harmonic confinement to $\omega_0 = 1$. In this case the ground-state (singlet) wave function is known analytically [141], and the total density can be expressed as [142]

$$\begin{aligned} \rho(r) &= \frac{4}{\pi(\sqrt{2\pi}+3)} \Big\{ e^{-r^2}(1 + r^2/2) + \frac{1}{2}\sqrt{\pi} e^{-3r^2/2} \times \\ &\times \Big[ I_0(r^2/2) + r^2 I_0(r^2/2) + r^2 I_1(r^2/2) \Big] \Big\}. \end{aligned} \tag{8.25}$$

The exact (spin) exchange-hole potential is simply

$$U_{N=2}^{x,\sigma}(\mathbf{r}) = -\int d\mathbf{r}' \frac{n_\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{8.26}$$

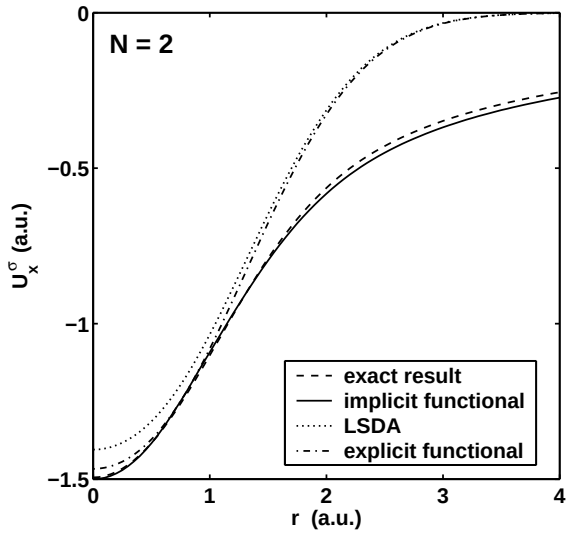


Figure 8.2: *Exchange-hole potential of a two-electron quantum dot calculated exactly (dashed line) and using the present model (solid line), LSDA (dotted line), and the present model in the 2DEG limit (dash-dotted line). The analytic density and orbitals are used as input for the model and the LSDA.*

In Fig. 8.2 we compare the exact exchange-hole potential (dashed line) to the result of our exchange model (solid line) and find an excellent agreement. We note that in a regime $0.75 \lesssim r \lesssim 0.85$ the parameter $y$ is not solvable from Eq. (8.17). Therefore, we set there $y$ to zero, which corresponds to the 2DEG result discussed above, i.e., we perform a well-valid LSDA-type approximation in this small regime. The dash-dotted line shows the result of our explicit density functional which corresponds to the 2DEG limit. This density functional has the wrong asymptotic behavior, but it is considerably closer to the exact result than the conventional LSDA (dotted line). In Fig. 8.3 we show the exchange-hole potentials for a 20-electron QD with $\omega_0 = 0.42168$, corresponding to a typical value of 5 meV in the effective-mass approximation when modeling QDs in GaAs [128, 129]. The exact-exchange (EXX) result (dashed line) is calculated here in the Krieger-Li-Iafrate (KLI) approach within spin-DFT implemented in the `octopus` real-space code [143]. Again, we find a very good agreement between EXX results and our model. However, despite the fact that $U_x^\sigma$ provided by the LSDA stays considerably above the EXX curve at $r \lesssim 4$, the opposite behavior at larger $r$ leads to a rather accurate LSDA exchange energy in the case of the $N = 20$ quantum dot. However, as seen in Table 8.1, in smaller QDs the performance of our exchange model is superior to the standard LSDA.

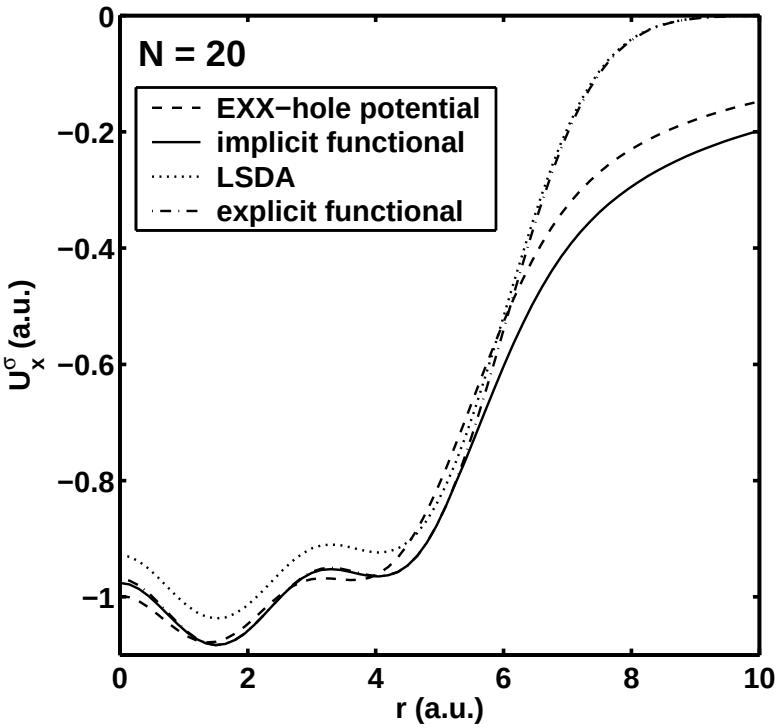


Figure 8.3: *Similar to Fig. 8.2 but here for 20 electrons. The exact-exchange result was calculated here using the KLI approximation.*

Table 8.1: *Exchange energies for different number of electrons calculated using the exact exchange, the implicit density functional of Sec. 8.1.1, standard LSDA, and the the explicit density functional of Sec. 8.1.2. For $N > 2$ the EXX result was calculated within the KLI approximation, and as input for our functionals and LSDA exchange we used the self-consistent density and orbitals from the standard LSDA including correlation ($\omega_0 = 1$ for $N = 2$, and $\omega_0 = 0.42168$ for $N > 2$).*

| N | EXX | Implicit functional | LSDA | Explicit functional |
|---|---|---|---|---|
| 2 | -1.0839 | -1.0836 | -0.983 | -1.026 |
| 6 | -2.229 | -2.284 | -2.130 | -2.223 |
| 12 | -4.890 | -5.059 | -4.763 | -4.972 |
| 20 | -8.781 | -9.124 | -8.632 | -9.012 |

## 8.3 Conclusions

We have provided new implicit and explicit exchange functionals that significantly improve the exchange-hole potentials and exchange energies for few electrons in 2D quantum dots with respect to the standard local density approximation. Our results also suggest that accurate approximations for the correlation energy functional can be developed analogously.

# Chapter 9

# General conclusions

In this thesis, we have shown that the ground state of interacting electrons with non-vanishing current and magnetization can be successfully described and investigated within density functional theories by employing approximate exchange-correlation energy functionals which depend explicitly on the Kohn-Sham spinors. This approach allows an unconstrained search of the Kohn-Sham ground state. As a consequence approximations such as the assumption of local or global collinearity between magnetization, current and corresponding conjugate fields are avoided. At the same time, other limitations of electron-gas based approximations, such as the divergences of the exchange-correlation potentials originating from the appearance of the Landau levels in the homogeneous electron-gas exposed to an external magnetic field are overcome in a natural way.

To make use of such spinor-orbital functionals, we have presented the derivation of the equations for the exchange-correlation components of the effective fields within the optimized effective potential method. Furthermore, a practical scheme for their solution and simplifying approximations have been suggested and analyzed. In this context, the relations, similarities and differences among different flavors of density functional theory have been elucidated.

We have confirmed that the solution of a long standing problem in density functional theory, which is the description of the degeneracy of ground states of open-shell systems carrying different paramagnetic-current densities, is achieved by using approximate orbital-dependent expressions for the exchange and correlation energy. In this context, we have derived a new expression for the correlation energy in the form of the Colle and Salvetti functional which takes into account the orbital currents of the Kohn-Sham ground state. The relevance of these terms has been evaluated.

We have then considered extended periodic systems and have calculated their orbital magnetic moments and band-splittings induced by the spin-orbit coupling. We have shown that, at the level of the exact-exchange-only approximation, the orbital magnetic moments are greatly underestimated. Thus we gave a clear indication that inclusion of correlation beyond of exact exchange is essential for these

quantities. On the other hand, the calculated band-splittings are in agreement with experimental results.

Important systems for technological applications are two-dimensional quantum dots. For these systems, we have shown that by adding to the exact-exchange approximation an ad-hoc self-interaction corrected correlation from the standard two-dimensional LSDA, total energies close to Quantum Monte Carlo results can be obtained.

However, for all the considered systems, we have found that the role of the exchange vector potential is minor. Our analysis also suggests that the same statement may be valid for the full exchange-correlation vector potential.

At last, motivated by the facts that three-dimensional functionals perform poorly when applied to two-dimensional systems – and that the development of functionals for the exchange and correlation energies of two-dimensional systems is still in its infancy – we derived new approximations for the exchange energy functional. Excellent agreement for the exchange-hole potentials and exchange energies is found when compared with the exact-exchange reference data for the two-dimensional uniform electron gas and few-electron quantum dots, respectively. Along the same lines models for the correlation-hole and thus approximations for the correlation energies could be obtained as well.

# Bibliography


[1] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

[2] E. Fermi, Accad. Naz. Lincei **6**, 602 (1927).

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

[4] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

[5] W. Kohn, in *Highlight of Condensed Matter Theory*, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985), p. 1.

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

[7] E.H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983).

[8] H. Englisch and R. Englisch, Phys. Stat. Solidi B **123**, 711 (1984).

[9] H. Englisch and R. Englisch, Phys. Stat. Solidi B **124**, 373 (1984).

[10] F. W. Averill and G. S. Painter, Phys. Rev. B **15**, 2498 (1992).

[11] S. G. Wang and W. H. E. Scharz, J. Chem. Phys. **105**, 4641 (1996).

[12] P. R. T. Schipper, O. V. Gritsenko, and E. J. Baerends, Theoret. Chim. Acta **99**, 4056 (1998).

[13] P. R. T. Schipper, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **111**, 4056 (1999).

[14] C. A. Ullrich and W. Kohn, Phys. Rev. Lett. **87**, 093001 (2001).

[15] R. van Leeuwen, Adv. in Q. Chem. **43**, 24 (2003).

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

[17] J. E. Harriman, Phys. Rev. A **24**, 680 (1981).

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

[19] S. V. Valone, J. Chem. Phys. **73**, 1344 (1980).

[20] J. T. Chayes, L. Chayes, and M. B. Ruskai, J. Stat. Phys **38**, 497 (1985).

[21] S. Pittalis and S. Kurth, in *Computational Condensed Matter Physics*, Vol. 32 of *Matter and Materials*, edited by S. Blügel *et al.* (Schriften des Forschungszentrums Jülich, Jülich, 2006), p. A03.

[22] S. Kurth and S. Pittalis, in *Computational Nanoscience: Do It Yourself!*, Vol. 31 of *NIC Series*, edited by J. Grotendorst, S. Blügel, and D. Marx (John von Neumann Institute for Computing, Jülich, 2006), p. 299.

[23] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[24] J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

[25] L. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[26] L. Sham and M. Schlüter, Phys. Rev. B **32**, 3883 (1985).

[27] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).

[28] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[29] A. D. Becke, J. Chem. Phys. **104**, 1040 (1996).

[30] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).

[31] J.P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999), ibid. **82**, 5179 (1999)(E).

[32] S. Kurth, J.P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).

[33] J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).

[34] A. Görling and M. Levy, Phys. Rev. B **47**, 13105 (1993).

[35] E. Engel, A. Höck, and R.M. Dreizler, Phys. Rev. A **61**, 032502 (2000).

[36] E.K.U. Gross, J.F. Dobson, and M. Petersilka, in *Density Functional Theory II*, Vol. 181 of *Topics in Current Chemistry*, edited by R.F. Nalewajski (Springer, Berlin, 1996), p. 81.

[37] *Time-Dependent Density Functional Theory*, edited by M.A.L. Marques *et al.* (Springer, Berlin Heidelberg, 2006), Vol. LNP 706.

[38] T. Grabo, T. Kreibich, S. Kurth, and E.K.U. Gross, in *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond Local Density Approximations*, edited by V. Anisimov (Gordon and Breach, Amsterdam, 2000), p. 203.

[39] S. Kümmel and J.P. Perdew, Phys. Rev. Lett. **90**, 043004 (2003).

[40] S. Kümmel and J.P. Perdew, Phys. Rev. B **68**, 035103 (2003).

[41] V. Sahni, J. Gruenebaum, and J.P. Perdew, Phys. Rev. B **26**, 4371 (1982).

[42] J.P. Perdew and M.R. Norman, Phys. Rev. B **26**, 5445 (1982).

[43] R. Sharp and G. Horton, Phys. Rev. **90**, 317 (1953).

[44] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[45] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **45**, 101 (1992).

[46] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **46**, 5453 (1992).

[47] O.V. Gritsenko and E.J. Baerends, Phys. Rev. A **64**, 42506 (2001).

[48] F. Della Sala and A. Görling, J. Chem. Phys. **115**, 5718 (2001).

[49] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[50] G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987).

[51] P. Skudlarski and G. Vignale, Phys. Rev. B **48**, 8547 (1993).

[52] G. Vignale and M. Rasolt, Phys. Rev. B **37**, 10685 (1988).

[53] K. Drese, Diploman thesis, Universität Wüzburg (1995).

[54] H. Saarikoski *et al.*, Phys. Rev. B **67**, 205327 (2003).

[55] A. Wensauer and U. Rössler, Phys. Rev. B **69**, 155302 (2004).

[56] N. Helbig, Diploman thesis, Universität Wüzburg (2001).

[57] N. Helbig, PhD thesis, Freie Universität Berlin (2006).

[58] O. Gunnarsson and B.I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[59] J. E. Eschrig and W. E. Pickett, Solid State Commun. **118**, 123 (2001).

[60] C. A. Ullrich, Phys. Rev. B **72**, 073102 (2005).

[61] K. Capelle and G. Vignale, Phys. Rev. Lett. **86**, 5546 (2001).

[62] K. Capelle and G. Vignale, Phys. Rev. B **65**, 113106 (2002).

[63] W. Kohn, A. Savin, and C.A. Ullrich, Int. J. Q. Chem **100**, 20 (2004).

[64] N.I. Gidopoulos, Phys. Rev. B **75**, 134408 (2007).

[65] K. Capelle, C. A. Ullrich, and G. Vignale, Phys. Rev. A **76**, 0125081 (2007).

[66] G. Diener, J. Phys.: Condens. Matter **3**, 9417 (1991).

[67] K. Capelle and E. K. U. Gross, Phys. Rev. Lett. **78**, 1872 (1996).

[68] S. Pittalis, S. Kurth, N. Helbig, and E. K. U. Gross, Phys. Rev. A **74**, 062511 (2006).

[69] S. Sharma *et al.*, Phys. Rev. Lett. **98**, 196405 (2007).

[70] T. Kreibich, S. Kurth, T. Grabo, and E.K.U. Gross, Adv. Quantum Chem. **33**, 31 (1999).

[71] J. Kübler, K. H Höck, J. Sticht, and A.R. Williams, J. Phys. F: Math. Phys. **18**, 469 (1988).

[72] T. Ziegler, A. Rauk, and E.J. Baerends, Theoret. Chim. Acta **43**, 261 (1977).

[73] U. von Barth, Phys. Rev. A **20**, 1693 (1979).

[74] F. Kutzler and G.S. Painter, Phys. Rev. B **43**, 6865 (1991).

[75] R. Merkle, A. Savin, and H. Preuss, J. Chem. Phys. **97**, 9216 (1992).

[76] E. J. Baerends, V. Branchadell, and M. Sodupe, J. Chem. Phys. **265**, 481 (1997).

[77] J. Tao and J.P. Perdew, Phys. Rev. Lett. **95**, 196403 (2005).

[78] A. D. Becke, J. Chem. Phys. **117**, 6935 (2002).

[79] J. Dobson, J. Chem. Phys. **98**, 8870 (1993).

[80] A. D. Becke and M. R. Roussel, Phys. Rev. A **39**, 3761 (1989).

[81] S. Maximoff, M. Ernzerhof, and G.E. Scuseria, J. Chem. Phys. **120**, 2105 (2004).

[82] S. Pittalis, S. Kurth, and E. K. U. Gross, J. Chem. Phys. **125**, 084105 (2006).

[83] S. Pittalis, S. Kurth, S. Sharma, and E. K. U. Gross, J. Chem. Phys. **127**, 124103 (2007).

[84] G. te Velde *et al.*, J. Comput. Chem. **22**, 931 (2001).

[85] E. Engel, in *A Primer in Density Functional Theory*, Vol. 620 of *Lecture Notes in Physics*, edited by C. Fiolhais, F. Nogueira, and M. Marques (Springer, Berlin, 2003), p. 56.

[86] T. H. Burgess, F. A.Bulat, and W. Yang, cond-mat/0610884.

[87] V. N. Staroverov and G. E. Scuseria, J. Chem. Phys. **125**, 081104 (2006).

[88] V. N. Staroverov and G. E. Scuseria, J. Chem. Phys. **124**, 141103 (2006).

[89] D. R. Rohr, O. V. Gritsenko, and E. J. Baerends, J. Mol. Structure: THEOCHEM **72**, 762 (2006).

[90] A. Hesselmann, A. W. Götz, F. Della Sala, and A. Görling, J. Chem. Phys. **127**, 054102 (2007).

[91] S. Ivanov, S. Hirata, and R.J. Bartlett, Phys. Rev. Lett. **83**, 5455 (1999).

[92] A. Görling, Phys. Rev. Lett. **83**, 5459 (1999).

[93] M. Seidl, J.P. Perdew, and S. Kurth, Phys. Rev. Lett. **84**, 5070 (2000).

[94] R. Colle and O. Salvetti, Theoret. Chim. Acta **37**, 329 (1975).

[95] R. Colle and O. Salvetti, Theoret. Chim. Acta **53**, 55 (1979).

[96] R. Colle and O. Salvetti, J. Chem. Phys. **79**, 1404 (1983).

[97] T. Grabo and E.K.U. Gross, Chem. Phys. Lett. **240**, 141 (1995).

[98] C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B **37**, 785 (1988).

[99] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[100] R. Singh, Lou Massa, and Viraht sahni, Phys. Rev. A **60**, 4135 (1999).

[101] J. Tao, P. Gori-Giorgi, J.P. Perdew, and R. McWeeny, Phys. Rev. A **63**, 032513 (2001).

[102] Y. Imamura and G.E. Scuseria, J. Chem. Phys. **116**, 6458 (2002).

[103] A. D. Becke and K. E. Edgecombe, J. Chem. Phys. **92**, 5397 (1990).

[104] T. Burnus, M.A.L. Marques, and E.K.U. Gross, Phys. Rev. A **71**, 010501 (2005).

[105] S. Sharma *et al.*, Phys. Rev. B **76**, 100401 (2007).

[106] N. Helbig *et al.*, arXiv:cond-mat/0605599 (2007).

[107] M. S. S. Brooks, Physica B **130**, 6 (1985).

[108] O. Eriksson, B. Johansson, and M.S.S. Brooks, J. Phys. Cond. Mat. **1**, 4005 (1989).

[109] O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 7311 (1990).

[110] L. Severin, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **71**, 7311 (1993).

[111] A. K. Rajagopal, J. Phys. C **11**, L943 (1978).

[112] A. H. Macdonald and S. H. Vosko, J. Phys. C: solid State Phys. **12**, 2977 (1979).

[113] H. Eschrig, G. Seifert, and Z. Ziessche, Solid State Commun. **56**, 777 (1985).

[114] H. Eschrig, M. Sargolzaei, K. Koepernik, and M. Richter, Europhys. Lett. **72**, 611 (2005).

[115] H. Ebert, M. Battocletti, and E.K.U. Gross, Europhys. Lett. **40**, 545 (1997).

[116] D. J. Singh and L. Nordström, *Planewaves pseudopotentials and the lapw method* (Springer, Berlin, 2005).

[117] J.K. Dewhurst, S. Sharma, and C. Ambrosch-Draxl, web-page: http://exciting.sourceforge.net, 2004.

[118] M. Singh, C. S. Wang, and J. Callaway, Phys. Rev. B **11**, 287 (1975).

[119] M. S. S. Brooks and P. J. Kelley, Phys. Rev. Lett. **51**, 1708 (1983).

[120] O. Eriksson *et al.*, Phys. Rev. B **67**, 205327 (2003).

[121] M. B. Stearns, in *Magnetic properties of 3d, 4d, and 5d elements, alloys and compounds*, edited by K. Hellwege and O. Madelung (Springer, Berlin, 1987), Vol. Vol. III/19a of Landolt-Boernstein, New Series.

[122] O. Madelung, *Semiconductors: Data Handbook* (Springer, Berlin, 2004).

[123] S. Rohra, E. Engel, and A. Görling, cond-mat/0608505 (2006).

[124] K. Bencheikh, J. Phys. A: Math. Gen. 36 11929-11936 (2003)

[125] Phys. Rev. Lett. **97**, 013005 (2006)

[126] S. Sharma, J.K. Dewhurst, and C. Ambrosch-Draxl, Phys. Rev. Lett. **95**, 136402 (2005).

[127] K. Capelle, G. Vignale, and B. Györffy, Phys. Rev. Lett. **87**, 206403 (2001).

[128] S. M. Reimann and M. Manninen, Rev. Mod. Phys. **74**, 1283 (2002).

[129] L. P. Kouwenhoven, D. G. Austing, and S. Tarucha, Rep. Prog. Phys. **64**, 701 (2001).

[130] C. Attaccalite, S. Moroni, P. Gori-giorgi, and G. Bachelet, Phys. Rev. Lett. **88**, 256601 (2002).

[131] W. Xin-Qiang, J. Phys.: Condens. Matter **12**, 4207 (2000).

[132] H. Stoll, E. Golka, and H. Preuss, Theor. Chim. Acta **55**, 29 (1980).

[133] A. K. Rajagopal and J. C. Kimball, Phys. Rev. B **15**, 2819 (1977).

[134] B. Tanatar and D. M. Ceperley, Phys. Rev. B **39**, 5005 (1989).

[135] C. Filippi, C. J. Umrigar, and M. Taut, J. Chem. Phys. **100**, 1290 (1994).

[136] Y. H. Kim *et al.*, Phys. Rev. B **61**, 5201 (200).

[137] L. Pollack and J. P. Perdew, J. Phys.: Condens. Matter **12**, 1239 (2000).

[138] S. Pittalis, E. Räsänen, N. Helbig, and E. K. U. Gross, Phys. Rev. B **76**, 235314 (2007)

[139] B. P. van Zyl, cond-mat/9907083 (1999).

[140] P. Gori-Giorgi, S. Moroni, and G. B. Bachelet, Phys. Rev. B **70**, 115102 (2004).

[141] M. Taut, J. Phys. A **27**, 1045 (1994).

[142] A. Wensauer, PhD Thesis, University of Regensburg (2003).

[143] A. Castro *et al.*, Phys. Stat. Sol. (b) **243**, 243 (2006).

# Publications

- S. Pittalis, E. Räsänen, N. Helbig, E.K.U. Gross *Exchange-Energy Functionals for finite Two-Dimensional Systems*, Phys. Rev. B **76**, 235314 (2007)
- S. Pittalis, S. Kurth, S. Sharma, E.K.U. Gross, *Orbital currents in the Colle-Salvetti correlation energy functional and the degeneracy problem*, J. Chem. Phys. **127**, 124103 (2007)
- S. Sharma, S. Pittalis, S. Kurth, S. Shallcross, J. K. Dewhurst, E. K. U. Gross *Comparison of exact-exchange calculations for solids in current-spin-density- and spin-density-functional theory*, Phys Rev. B **76**, 100401 (2007) (Rapid. Comm.)
- S. Sharma J. K. Dewhurst, C. Ambrosch-Draxl, S. Kurth, N. Helbig, S. Pittalis, E. K. U. Gross, S. Shallcross, L. Nordström, *First-Principles Approach to Noncollinear Magnetism: Towards Spin Dynamics*, Phys. Rev. Lett. **98**, 196405 (2007)
- N. Helbig, S. Kurth, S. Pittalis, E. Räsänen, E.K.U. Gross, *Exchange-correlation orbital functionals in current-density-functional theory: Application to a quantum dot in magnetic fields*, arXiv:cond-mat/0609696, submitted to Phys. Rev. B (2007)
- S. Pittalis, S. Kurth, E.K.U. Gross *On the degeneracy of atomic states within exact-exchange (spin-) density functional theory*, J. Chem. Phys. **125**, 084105 (2006)
- S. Pittalis, S. Kurth, N. Helbig, E.K.U. Gross, *Optimized Effective Potentials Method in Current-Spin-Density Functional Theory*, Phys. Rev. A **74**, 062511 (2006)
- S. Pittalis, S. Kurth, *The Optimized Effective Potential Method* in "Computational Condensed Matter Physics", Ed. by S. Blügel, G. Gompper, E. Koch, H. Müller-Krumbhaar, R. Spatschek, R.G. Winkler, Schriften des Forschunsgzentrums Jülich, Matter and Materials Vol. **32** (2006).
- S. Kurth, S. Pittalis, *Optimized Effective Potential Method and LDA+U* in "Computational Nanoscience: Do It Yourself!", Ed. by J. Grotendorst, S. Blügel, D. Marx, NIC Series Vol. **31** (2006)

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